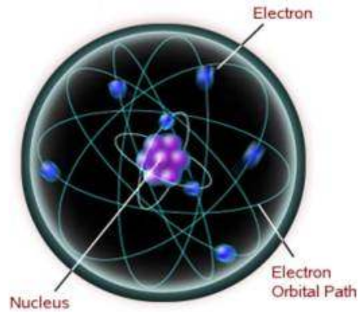
Free electron model

- A free electron model is the simplest way to represent the electronic structure of metals.
- Although the free electron model is a great oversimplification of the reality, surprisingly in many cases it works pretty well, so that it is able to describe many important properties of metals.
- According to this model, the valence electrons of the constituent atoms of the crystal become conduction electrons and travel freely throughout the crystal.
- Therefore, within this model we neglect the interaction of conduction electrons with ions of the lattice and the interaction between the conduction electrons.
- In this sense we are talking about a *free electron gas*.
- However, there is a principle difference between the free electron gas and ordinary gas of molecules.

- First, electrons are charged particles.
- Therefore, in order to maintain the *charge neutrality* of the whole crystal, we need to include positive ions.
- This is done within the *jelly model*, according to which the positive charge of ions is smeared out uniformly throughout the crystal.
- This positive background maintains the charge neutrality but does not exert any field on the electrons.
- Ions form a uniform jelly into which electrons move.
- Second important property of the free electron gas is that it should meet the Pauli exclusion principle, which leads to important consequences.

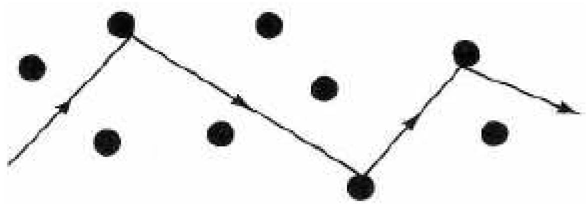
Electronic Transport
-Drude model-



- The simplest treatment of the electrical conductivity was given by Drude.
- There are four major assumptions within the Drude model.

1. Electrons are treated as classical particles within a free-electron approximation.
   - Thus, in the absence of external electromagnetic fields each electron is taken to move uniformly in a straight line, neglecting the interactions with other electrons and ions.
   - In the presence of external fields each electron is taken to move according to Newton's laws of motion.

2. Electrons move free only between collisions with scattering centers.
   - Collisions, as in kinetic theory, are instantaneous events that abruptly alter the velocity of an electron.
   - Drude attributed them to the electrons scattering by ion cores.
   - However, this is not a correct picture of electron scattering on ordered periodic structures.
   - A particular type of scattering centers does not matter in the Drude model.
   - An understanding of metallic conduction can be achieved by simply assuming that there is *some* scattering mechanism, without inquiring too closely into just what that mechanism might be.



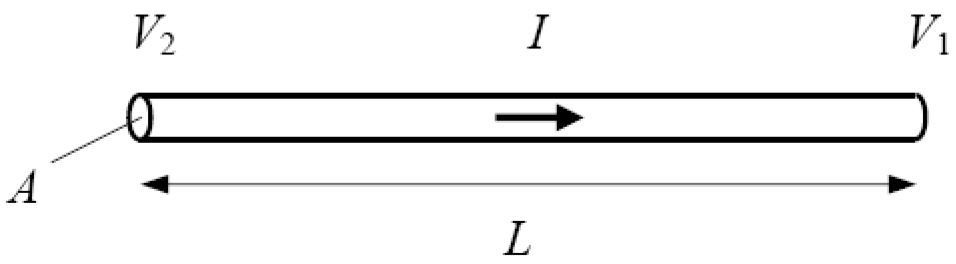
Trajectory of a conduction electron scattering off the ions, according to the picture of Drude.

3. An electron experiences a collision, resulting in an abrupt change in its velocity, with a probability per unit time $1/\tau$.
   - The time τ is an average time between the two consecutive scattering events.
   - It known as, the *collision time* (relaxation time), it plays a fundamental role in the theory of metallic conduction.
   - It follows from this assumption that an electron picked at random at a given moment will, on the average, travel for a time τ before its next collision.
   - The relaxation time τ is taken to be independent of an electron's position and velocity.

4. Electrons are assumed to achieve thermal equilibrium with their surroundings only through collisions.
   - These collisions are assumed to maintain local thermo-dynamic equilibrium in a particularly simple way: immediately after each collision an electron is taken to emerge with a velocity that is not related to its velocity just before the collision, but randomly directed and with a speed appropriate to the temperature prevailing at the place where the collision occurred.

Now we consider the application of the Drude model for electrical conductivity in a metal.

- According to *Ohm's law,* the current *I* flowing in a wire is proportional to the potential drop $V=V_2-V_1$ along the wire: $V = IR$, where R, the resistance of the wire, depends on its dimensions.
- It is much more convenient to express the *Ohm's law* in a form which is independent of the dimensions of the wire because these factors are irrelevant to the basic physics of the conduction.



- We define the conductivity which is the proportionality constant between the current density **j** and the electric field **E** at a point in the metal:

$$\mathbf{j}=\sigma\mathbf{E}$$

- The current density **j** is a vector, parallel to the flow of charge, whose magnitude is the amount of charge per unit time crossing a unit area perpendicular to the flow.
- Thus if a uniform current I flows through a wire of length L and cross-sectional area A, the current density will be $\mathbf{j} = I/A$.
- Since the potential drop along the wire will be $V = EL$, $\mathbf{j}=\sigma\mathbf{E}$ gives $I/A= \sigma V/L$, and hence $R = L/ \sigma A = \rho L/A$, where we introduced resistivity $\rho =1/ \sigma$.
- Unlike R, σ and ρ, is a property of the material, since it does not depend on the shape and size.

-Current Density-

The number of subatomic particles per unit time crossing a unit area in a plane perpendicular to the direction of movement of the particles.

- Now we want to express σ is terms of the microscopic properties using the Drude model.
- If *n* electrons per unit volume all move with velocity **v**, then the current density they give rise to will be parallel to **v**.
- Furthermore, in a time *dt* the electrons will advance by a distance v*dt* in the direction of v, so that *n*(v*dt*)*A* electrons will cross an area *A* perpendicular to the direction of flow.
- Since each electron carries a charge -*e*, the charge crossing *A* in the time *dt* will be -*nevAdt*, and hence the current density is

$$\mathbf{j} = -ne\mathbf{v}$$

11 Free Electron Fermi Gas

11.1 Electrons in metals

- Characteristics of metals

1. Metals obey Ohm law that can be written as

$$\boldsymbol{J} = \sigma \boldsymbol{E}$$

where $\boldsymbol{J}$ is the current density (Am^{-2})

σ is the electrical conductivity ($\Omega^{-1}m^{-1}$)

$\boldsymbol{E}$ is the electric field gradient (Vm^{-1})

For metals, $\sigma = 10^{6} \rightarrow 10^{8}\ \Omega^{-1}m^{-1}$

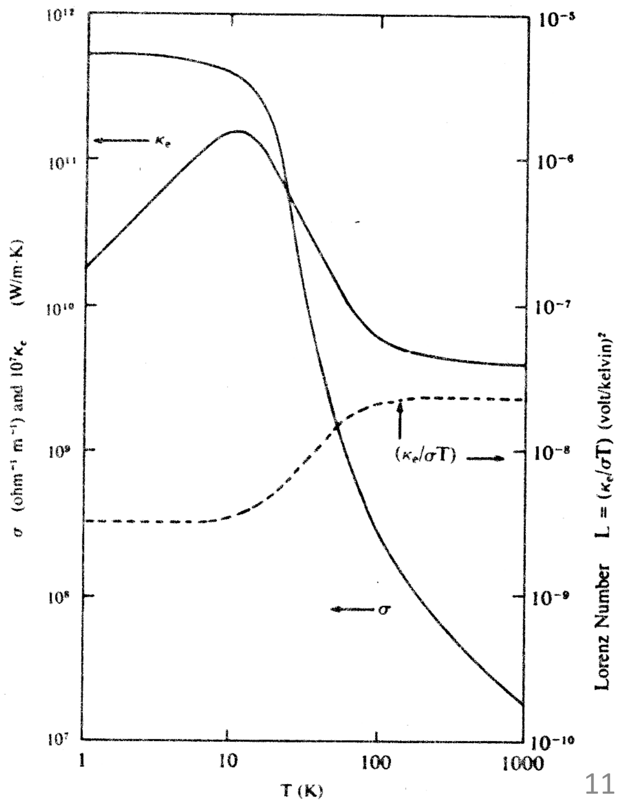
For insulators, $\sigma \approx 10^{-16}\ \Omega^{-1}m^{-1}$

For semiconductors, $\sigma = 10^{-4} \rightarrow 10^{5}\ \Omega^{-1}m^{-1}$

2. Metals have high electronic thermal conductivity K_e

   Metals that have good thermal conductivity are also good electrical conductors – the Wiedemann-Franz law of (K_e/σ)

3. At sufficiently low temperatures, σ reaches a high plateau value which is contributed by impurities and lattice imperfections, such as shown by Cu

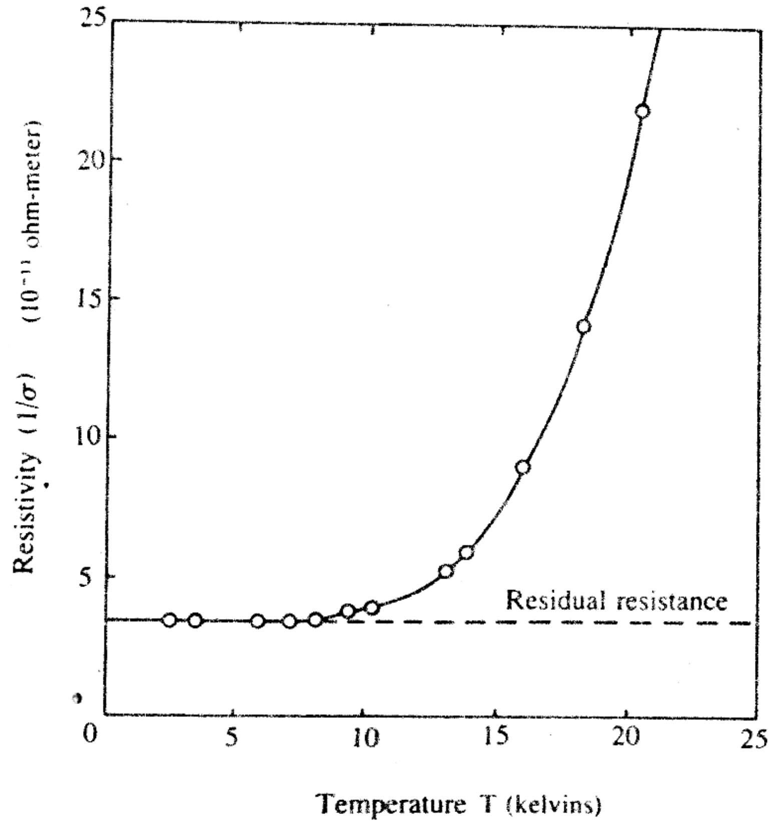


4. For a metal, the electrical resistivity (inverse of electrical conductivity), ρ (Ωm), follows the Matthiessen rule, whereby the contribution by impurities and lattice imperfections is the same for all temperatures

$$\rho(T) = \frac{1}{\sigma(T)} = \frac{1}{\sigma_{\substack{impurities \\ and\ lattice \\ imperfections}}} + \frac{1}{\sigma_{pure}(T)}$$

At sufficiently low temperatures and if $\sigma_{pure}(T) \to \infty$, then $\sigma_{impurities\ and\ lattice\ imperfections}$ becomes the main component (constant value)

Thus electrical conductivity ρ(low T) has a constant value

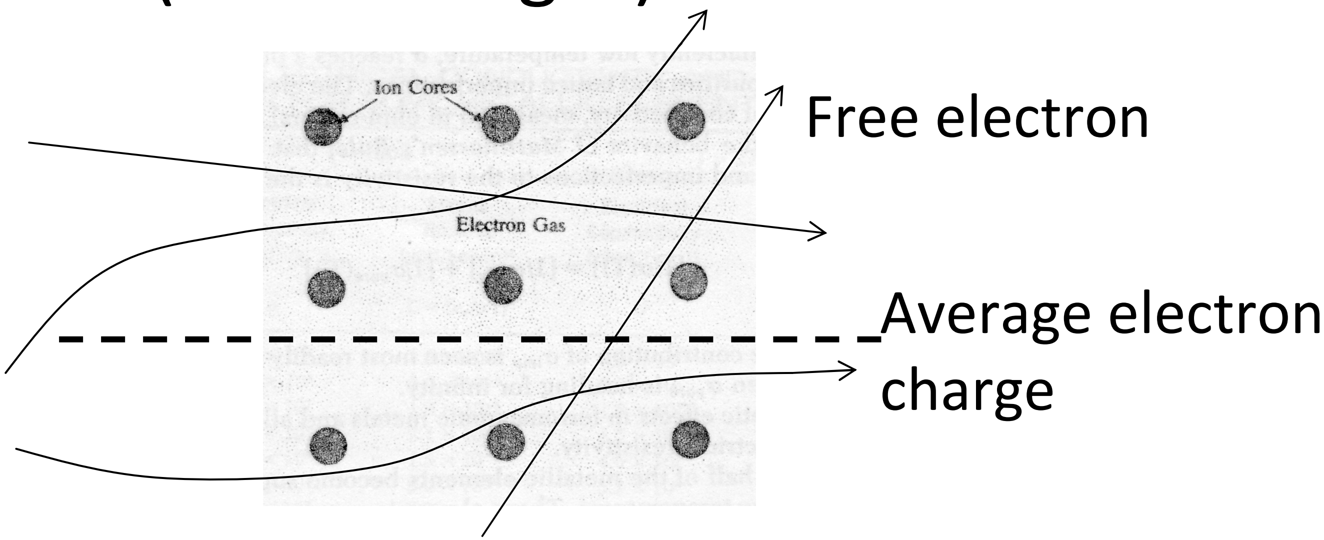


5. Magnetic effects in metals of ferromagnets and alloys also contribute to electrical resistivity

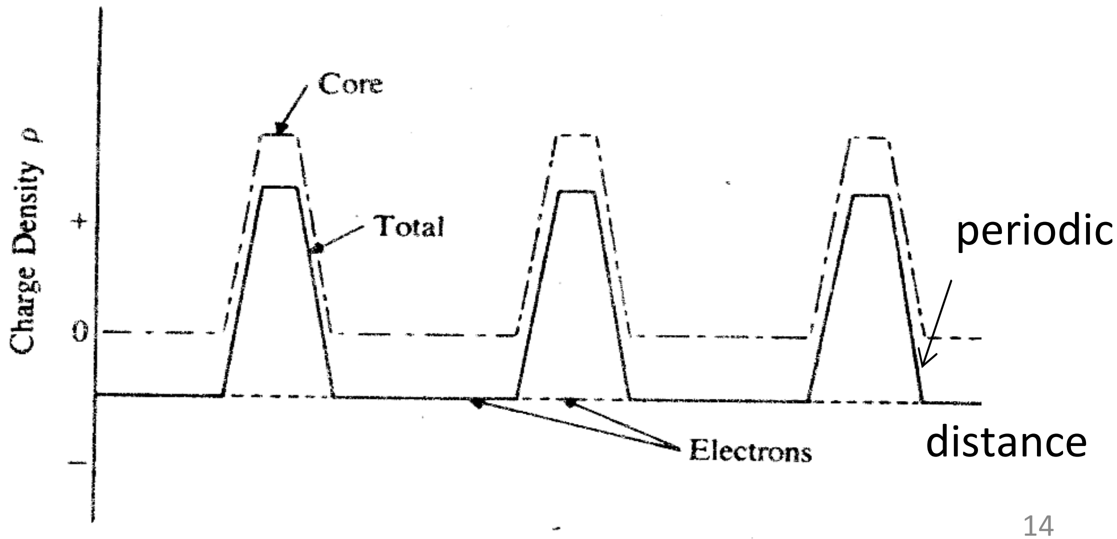
6. Free electron gas in metals has a small electronic specific heat, $C_e \propto T$ (small value)

11.2 Free electrons and positive ion cores

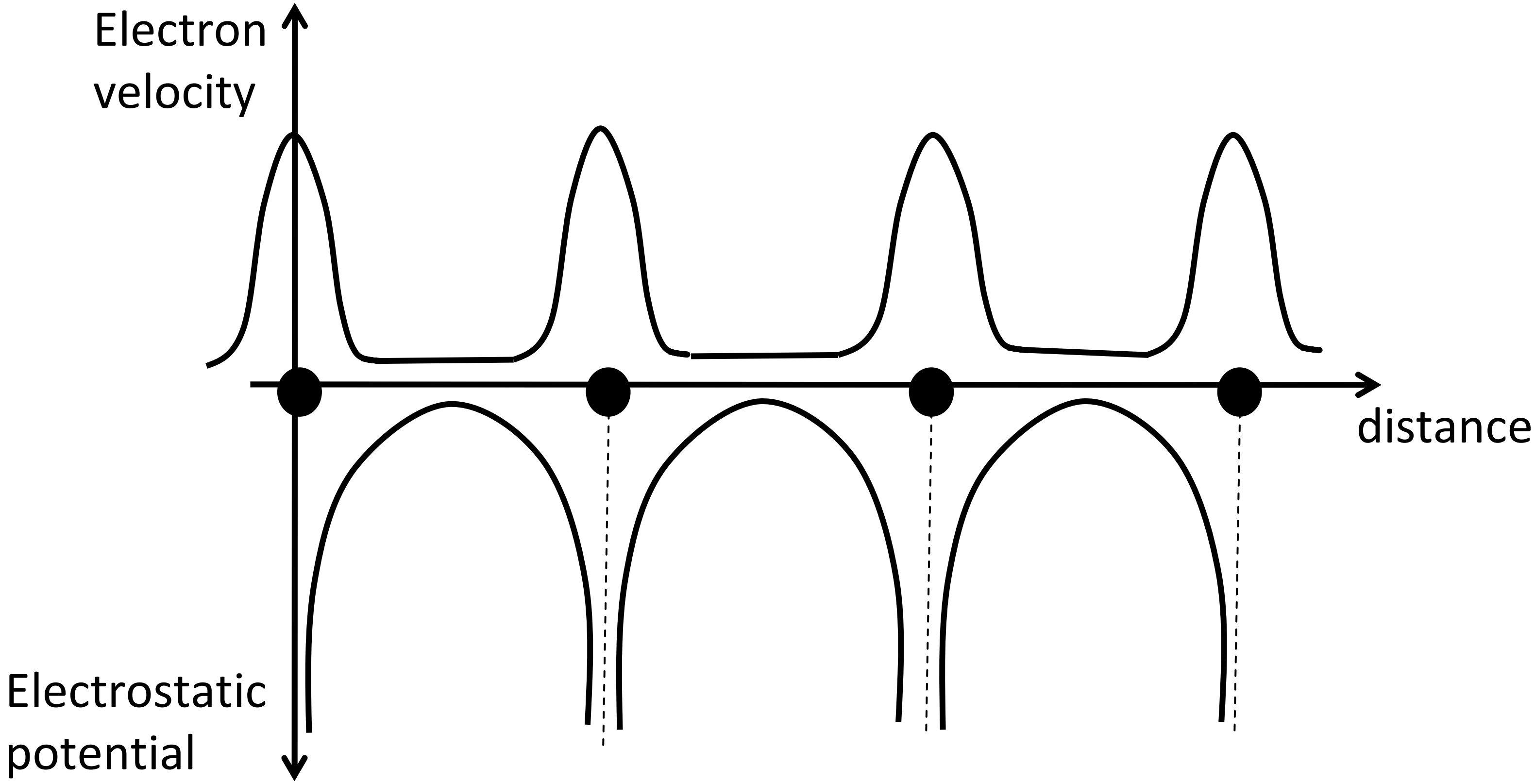
- Free electrons (electrons gas) formed metal binding



- Charge density



- Electrostatic potential and electron velocity



- Electron velocity increases to a maximum value close to ion cores because of the decrease in electrostatic potential

- Thus the electrons stay longer between the ion cores
- The conduction electrons are not deflected by the ion cores because particle wave propagation is free in periodic lattices (for example by X-rays)
- A conduction electron is not scattered by other conduction electrons due to Pauli Exclusion Principle
- Electrons in a free electron Fermi gas are free to move and do not interact with each other according to the Pauli principle (two electrons cannot have the same quantum numbers)

11.3 Classical theories for free electron gas

- Drude model
  - Each electron has kinetic energy $(3/2)k_BT$, moving with the same thermal velocity
  - Thus the total kinetic energy for *N* electrons is

$$Kinetic\ energy = (3/2)Nk_BT$$

  - The electronic specific heat is

$$C_e = (3/2)Nk_B$$

- Lorentz model
  - The electrons have different thermal velocity

- Using Boltzmann equation, the kinetic energy is

  $$Kinetic\ energy = (3/2)Nk_BT$$

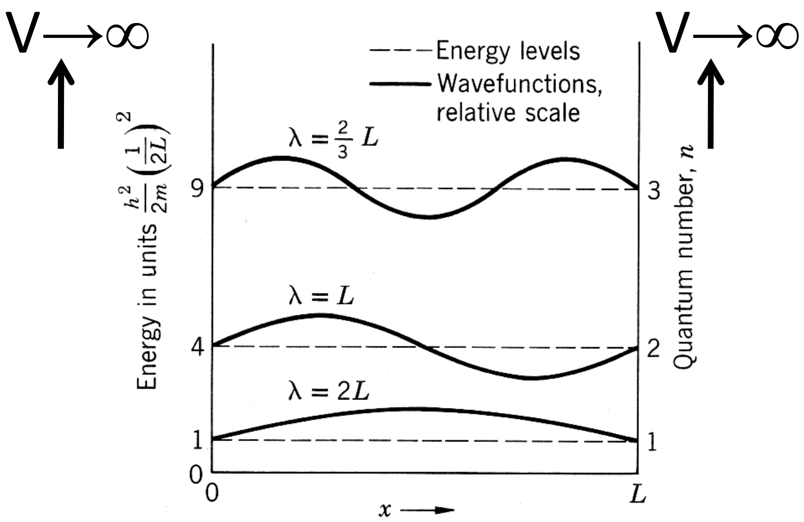
- The electronic specific heat is

  $$C_e = (3/2)Nk_B$$

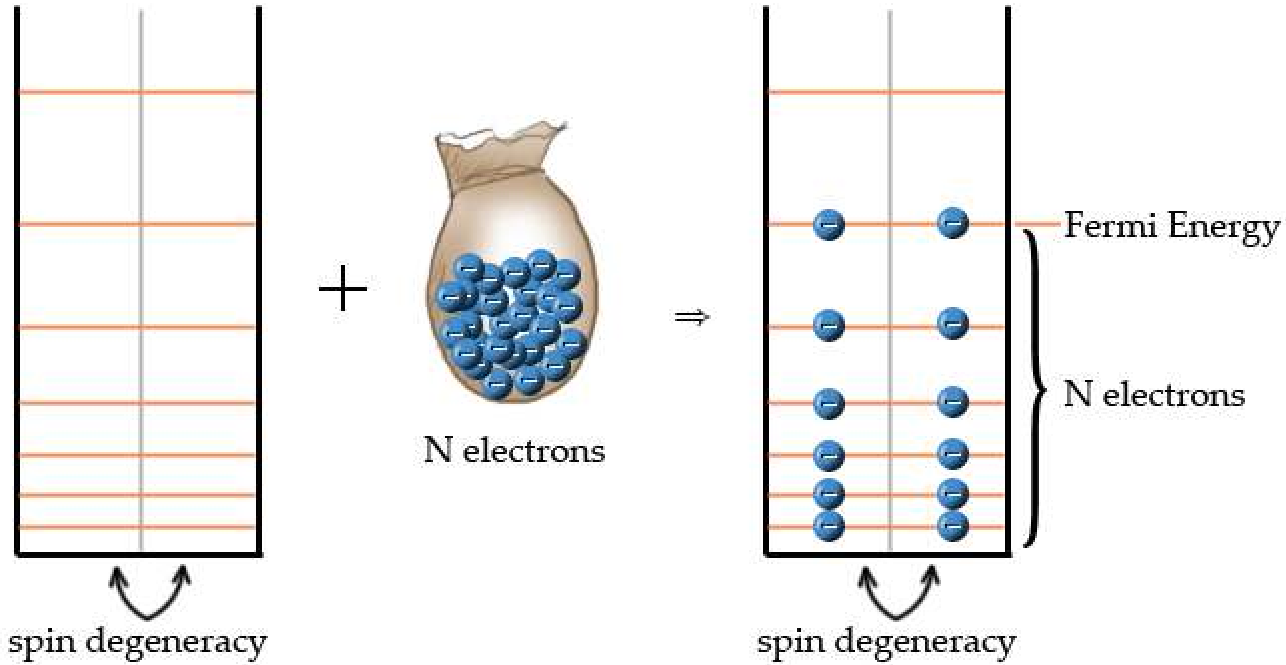
- Failures of classical theories
- Values of C_e are too high
- The mean free paths of electrons are also too high compared to the distance between atoms
- The solution is to use Pauli Exclusion Principle (quantized theory)

11.4 Quantized free electron gas theory

- Consider a free electron gas in 1-dimension where the potential energy is zero
- Thus the total energy is contributed only by the kinetic energy of the electrons
- The electron of mass *m* is inside an infinite potential barrier of length *L*



Fermi Energy
-Basic idea-



- The wave function $\psi_n(x)$ for the electron in the barrier is a solution of the Schrödinger equation

$$\hat{H}\psi_n = E_n\psi_n$$

where the Hamiltonian operator is

$$\hat{H} = \frac{\hat{p}^2}{2m} \qquad \text{(kinetic energy)}$$

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}$$

- Therefore

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_n}{\partial x^2} = E_n\psi_n \qquad (11.1)$$

- The solution for ψ_n can be written as

$$\psi_n(x) = A\sin\left(\frac{2\pi}{\lambda_n}x\right) \tag{11.2}$$

where $2\pi/\lambda_n$ is the wave vector

- Boundary conditions at $x = 0$ and $x = L$ give

$$\psi_n(0) = 0 = \psi_n(L) = A\sin\left(\frac{2\pi}{\lambda_n}L\right)$$

$$\sin\left(\frac{2\pi}{\lambda_n}L\right) = 0$$

$$\frac{2\pi}{\lambda_n}L = n\pi \qquad n = 1,2,3\ldots$$

$$\frac{2\pi}{\lambda_n} = \frac{n\pi}{L} \tag{11.3}$$

- Substitute Eq. (11.2) into Eq. (11.1) and use Eq. (11.3) to obtain the energy

$$-\frac{\hbar^2}{2m}\cdot-\left(\frac{2\pi}{\lambda_n}\right)^2\psi_n = E_n\psi_n$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_n}{\partial x^2} = E_n\psi_n$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{\lambda_n}\right)^2$$

$$\psi_n(x) = A\sin\left(\frac{2\pi}{\lambda_n}x\right)$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \qquad (11.4)$$

where E_n is the energy for level *n*

- This energy is for the case of one electron

- Let us say that there are N electrons
- The quantum numbers for an electron orbit are n and m_s where n is a positive integer and m_s = +½ (spin ↑) or -½ (spin ↓)
- So a pair of electron orbits that have the same quantum number n, according to Pauli Exclusion Principle, can have two electrons with spin ↑ and spin ↓
- If n_F is the highest level filled by electrons

$n = n_F$ ——— (2)

$n = 3$ ——— (2)

$n = 2$ ——— (2)

$n = 1$ ——— ← Fill in electrons (2)

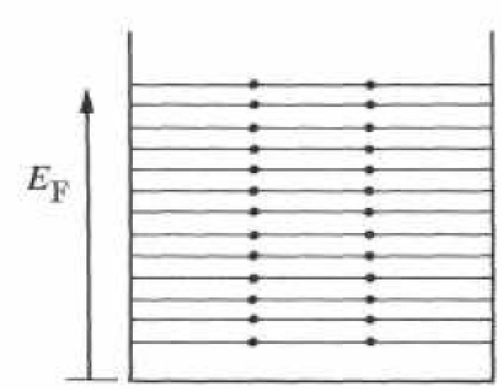
$2n_F$ = N electrons

- Energy at level n_F is

$$E_F = \frac{\hbar^2}{2m}\left(\frac{n_F\pi}{L}\right)^2$$

$$E_F = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2 \qquad \text{(1-dimension)} \qquad (11.5)$$

- E_F is called the Fermi energy, which is the highest level energy that is filled by electrons in the ground state
- In metals the value of the Fermi energy is of the order of 5 eV.
- The ground state of the N electron system is illustrated in Figure below:
  - All the electronic levels are filled up to the Fermi energy.
  - All the levels above are empty.



11.5 In 3-dimension

- The Schrödinger equation for free electrons is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_{\boldsymbol{k}}(\boldsymbol{r}) = E_{\boldsymbol{k}}\psi_{\boldsymbol{k}}(\boldsymbol{r}) \qquad (11.6)$$

- If the electrons are in a cube of sides *L*, then the wave functions are quantized stationary waves (obeying the Schrödinger equation)

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = A\sin\left(\underbrace{\frac{n_x\pi}{L}}_{k_x}x\right)\sin\left(\underbrace{\frac{n_y\pi}{L}}_{k_y}y\right)\sin\left(\underbrace{\frac{n_z\pi}{L}}_{k_z}z\right) \qquad (11.7)$$

where n_x, n_y and n_z are positive integers

- The wave functions in 3-dimension must also fulfill the periodic boundary conditions, for example for the *x* coordinate

$$\psi(x + L, y, z) \equiv \psi(x, y, z) \qquad (11.8)$$

with period *L* in the *x* direction

- The same goes for coordinates *y* and *z*
- The wave functions that obey Schrödinger equation and periodic condition are of the form

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = exp(i\boldsymbol{k} \cdot \boldsymbol{r}) \qquad (11.9)$$

if the wave vector components ***k*** obey

$$k_x, k_y, k_z = 0, \pm\frac{2\pi}{L}, , \pm\frac{4\pi}{L} \dots \qquad (11.10)$$

- Meaning that each ***k*** **component** has the form $\frac{n2\pi}{L}$ where *n* is a positive or negative integer

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- Exercise: Using Eq. (11.9) show that Eq. (11.10) obeys Eq. (11.8)

▪ For the *x* component

$$exp(ik_x(x+L)) = exp\left(i\frac{n2\pi}{L}(x+L)\right)$$

$$= exp\left(i\frac{n2\pi}{L}x\right)\underbrace{exp(in2\pi)}_{1}$$

$$= exp\left(i\frac{n2\pi}{L}x\right)$$

$$\boxed{\psi_{\boldsymbol{k}}(\boldsymbol{r}) = exp(i\boldsymbol{k}\cdot\boldsymbol{r})}$$

$$\boxed{k_x, k_y, k_z = 0, \pm\frac{2\pi}{L},, \pm\frac{4\pi}{L}\ldots}$$

$$exp\left(ik_x(x+L)\right) = exp(ik_x x)$$

- Thus

$$\psi(x+L) = \psi(x)$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_{\boldsymbol{k}}(\boldsymbol{r}) = E_{\boldsymbol{k}}\psi_{\boldsymbol{k}}(\boldsymbol{r})$$

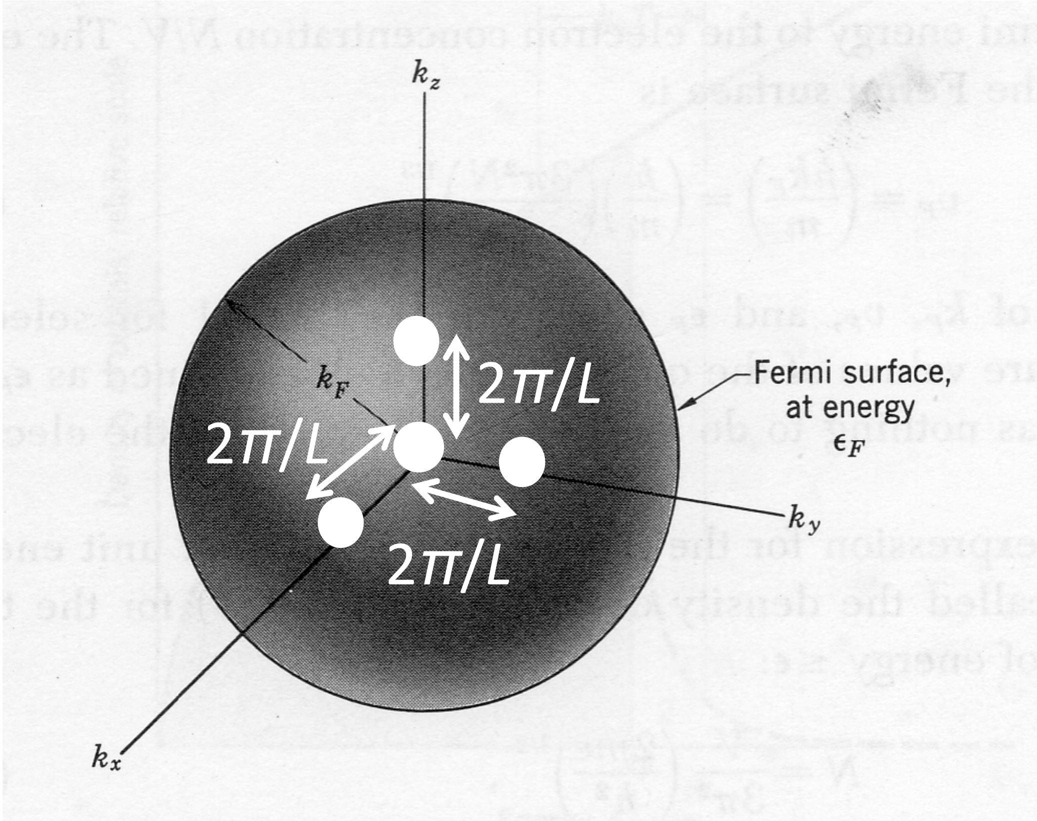
$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = exp(i\boldsymbol{k}\cdot\boldsymbol{r})$$

- Similarly for components *y* and *z*

- Substitution of Eq. (11.9) into Eq. (11.6) gives

$$E_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2\left(k_x^2+k_y^2+k_z^2\right)}{2m} \qquad (11.11)$$

- In the ground state, the orbits that are filled by *N* free electrons can be represented by points in a sphere which is in the ***k*** space



- The energy at the surface of the sphere (Fermi surface) is called Fermi energy

$$E_F = \frac{\hbar^2}{2m} k_F^2 \qquad (11.12)$$

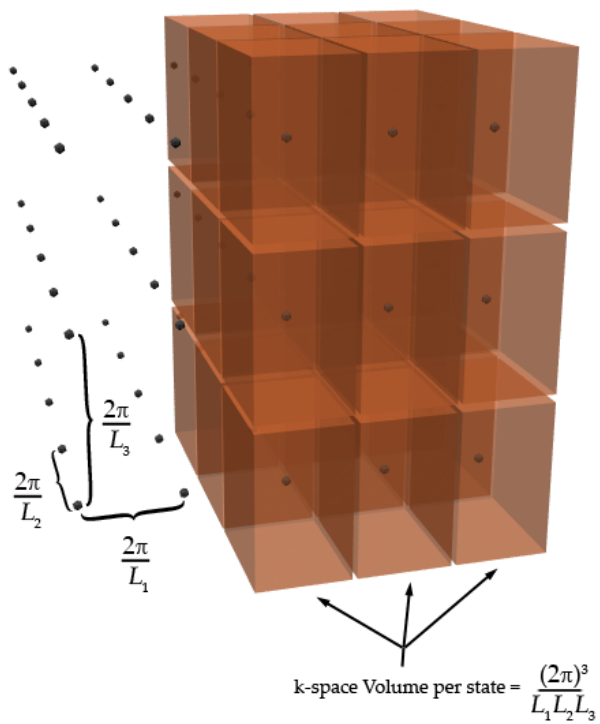
where k_F is the wave vector at the Fermi surface

Fermi Energy & Wavevector

- The Fermi energy and the Fermi wavevector (momentum) are determined by the number of valence electrons in the system.
- In order to find the relationship between N and k_F, we need to count the total number of orbitals in a sphere of radius k_F which should be equal to N.
- There are two available spin states for a given set of k_x, k_y, and k_z.
- The volume in the **k** space which is occupies by this state is equal to $(2\pi / L)^3$.

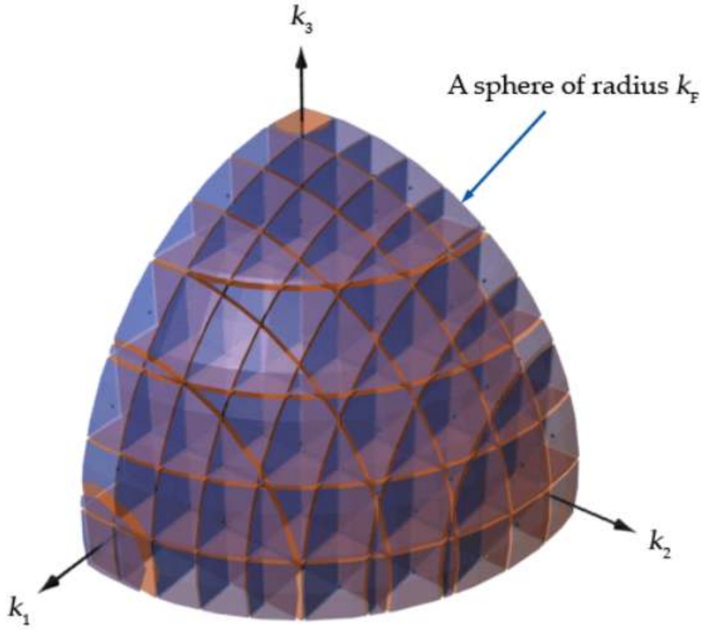
If we have N electrons, and put them into the system, what will be the highest occupied energy?

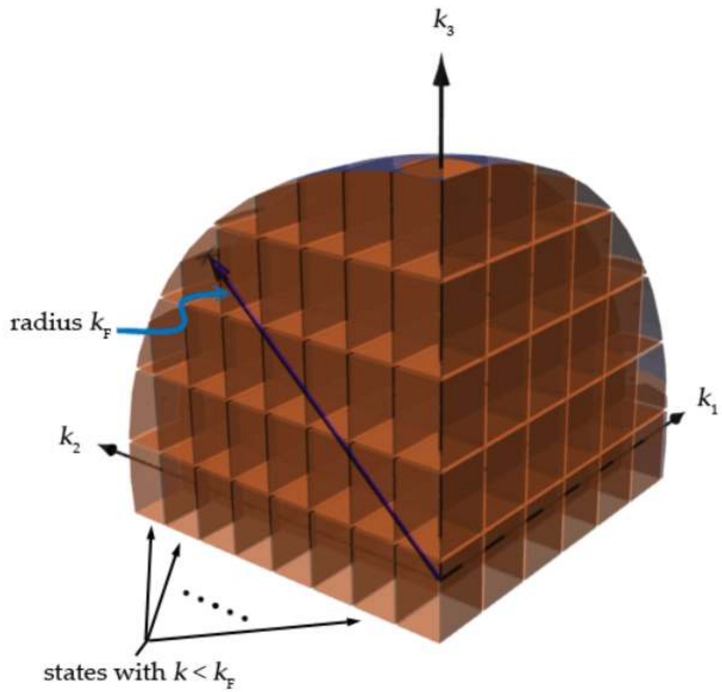
k-space Volume of a single electron (ignoring spin):



k-space Volume of a sphere $k < k_F$: $\hat{V}_{k \leq k_F} = \dfrac{4\pi k_F^3}{3}$

States σ with $k < k_F$: $\sigma_{k \leq k_F} = g \cdot \dfrac{\hat{V}_{k \leq k_F}}{\hat{V}_{state}}$, where g is the degeneracy due to spins (=2).





- So, for a volume $(2\pi/L)^3$ in k space, there is only one set of wave vectors (for one point) that is allowed, which is the triplet k_x, k_y and k_z
- Therefore in a sphere of volume $(4/3)\pi k_F^3$, the total number of orbits is

$$\frac{(4/3)\pi k_F^3}{(2\pi/L)^3}$$

- While the number of electrons is

$$2\cdot\frac{(4/3)\pi k_F^3}{(2\pi/L)^3}=\frac{V}{3\pi^2}k_F^3=N \qquad (11.13)$$

- The factor 2 is due to the two values for m_s (the quantum number for spin) for each allowed $\boldsymbol{k}$
- Therefore

$$k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3}$$

$$E_F = \frac{\hbar^2}{2m} k_F^2$$

$$k_F = (3\pi^2 n)^{1/3} \qquad (11.14)$$

where $\boldsymbol{n = N/V}$ is the electron concentration

- Thus k_F is dependent on the concentration of free electrons and Fermi energy becomes

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \qquad (11.15)$$

- The electron velocity on the Fermi surface is

$$\upsilon_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}(3\pi^2 n)^{1/3} \qquad (11.16)$$

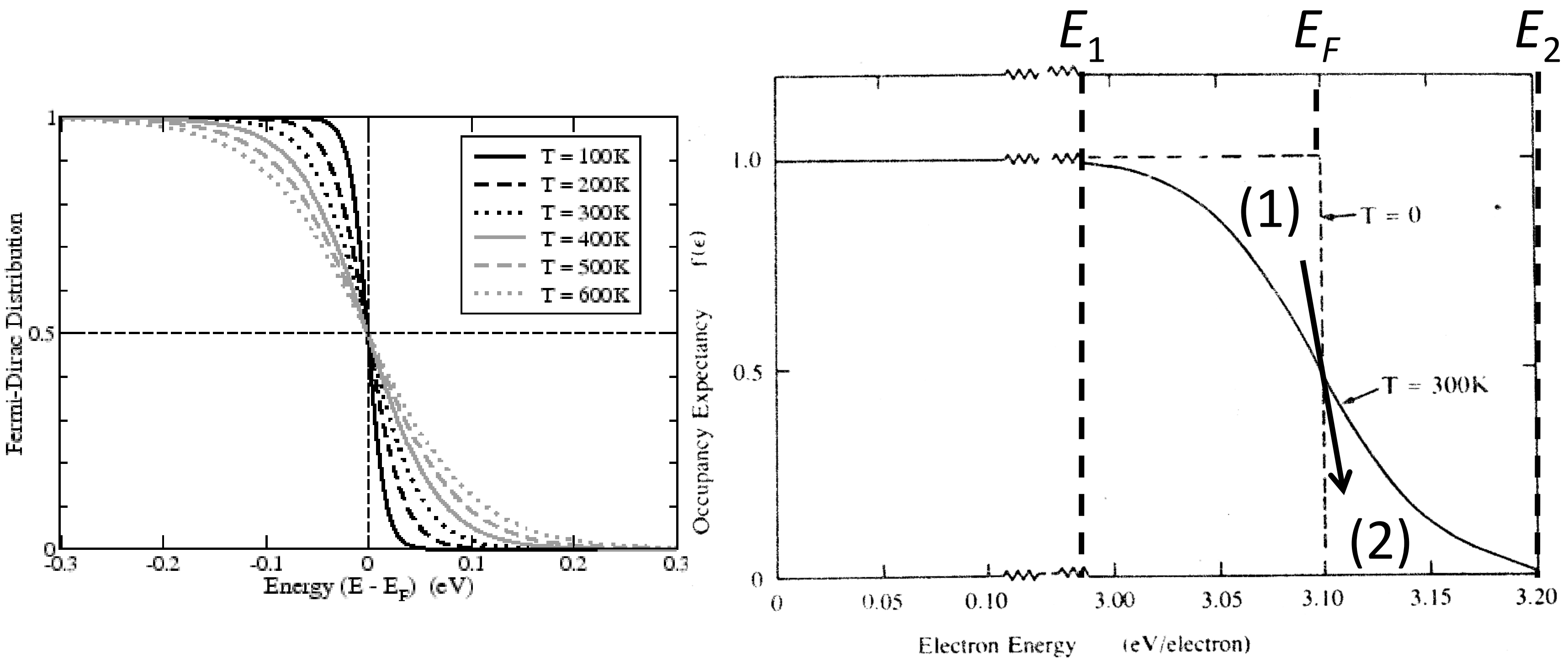
- Some values for $n=N/V$, k_F, υ_F, E_F and $T_F=E_F/k_B$ (Fermi temperature)

Metal	$n\times10^{22}$ (cm^{-3})	$k_F\times10^{8}$ (cm^{-1})	$\upsilon_F\times10^{8}$ (cms^{-1})	E_F (eV)	$T_F\times10^{4}$ (K)
Na	2.65	0.92	1.07	3.23	3.75
Cu	8.45	1.36	1.57	7.00	8.12
Zn	13.10	1.57	1.82	9.39	10.90
Al	18.06	1.75	2.02	11.63	13.49

11.6 Fermi-Dirac distribution

- The Fermi-Dirac distribution, $f(E)$, for an ideal electron gas gives the occupancy expectancy by electrons of an orbit of energy E

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1} \qquad (11.17)$$



Fermi-Dirac distribution

- This is the ground state of the *N* electron system at absolute zero.
- What happens if the temperature is increased?
- The kinetic energy of the electron gas increases with temperature.
- Therefore, some energy levels become occupied which were vacant at zero temperature, and some levels become vacant which were occupied at absolute zero.
- The distribution of electrons among the levels is usually described by the *distribution function*, $f(E)$, which is defined as the probability that the level E is occupied by an electron.
- Thus if the level is certainly empty, then, $f(E) = 0$, while if it is certainly full, then $f(E) = 1$.
- In general, $f(E)$ has a value between zero and unity.

- At absolute zero temperature, $T = 0$ K
- Occupation of orbit is complete till energy $E = E_F$

$$f(E) = 1 \text{ for } E < E_F$$
$$\quad = 0 \text{ for } E > E_F$$

- At temperatures $T > 0$ K
- Occupation of orbit is complete till energy $E_1 < E_F$
- Occupancy expectancy is zero for energy $E_2 > E_F$
- $f(E) = 1/2$ when $E = E_F$ *at 300K*
- The kinetic energy of electrons increases with the increase in temperature
- Transfer of electrons from region (1) to (2)

- When the system is heated (T>0°K), thermal energy excites the electrons.
- However, all the electrons do not share this energy equally, as would be the case in the classical treatment, because the electrons lying well below the Fermi level E_F cannot absorb energy.
- If they did so, they would move to a higher level, which would be already occupied, and hence the exclusion principle would be violated.

- Recall in this context that the energy which an electron may absorb thermally is of the order $k_B T$ (= 0.025 eV at room temperature), which is much smaller than E_F, this being of the order of 5 eV.
- Therefore only those electrons close to the Fermi level can be excited, because the levels above E_F are empty, and hence when those electrons move to a higher level there is no violation of the exclusion principle.
- Thus only these electrons which are a small fraction of the total number - are capable of being thermally excited.

- The distribution function at non-zero temperature is given by the *Fermi distribution function*.
  - The derivation WILL NOT BE presented here.
- The Fermi distribution function determines the probability that an orbital of energy *E* is occupied at thermal equilibrium

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

- The quantity μ is called the chemical potential.
- The chemical potential can be determined in a way that the total number of electrons in the system is equal to *N*.
- At absolute zero $\mu = E_F$.

An important quantity which
characterizes electronic properties
of a solid is the *density of states*,
which is the *number of electronic states*
per unit energy range.

11.7 Density of states, $D(E)$, for electrons

- Compare with the density of states, $g(\omega)$, for phonons
- The density of states $D(E)$ for electrons is the number of filled orbits in per unit range of energy
- Total number of orbits that has energy $\leq E$ is (from Eq. (11.15))

$$N = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

$$\boxed{E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}} \qquad (11.18)$$

- The density of states (orbits) is

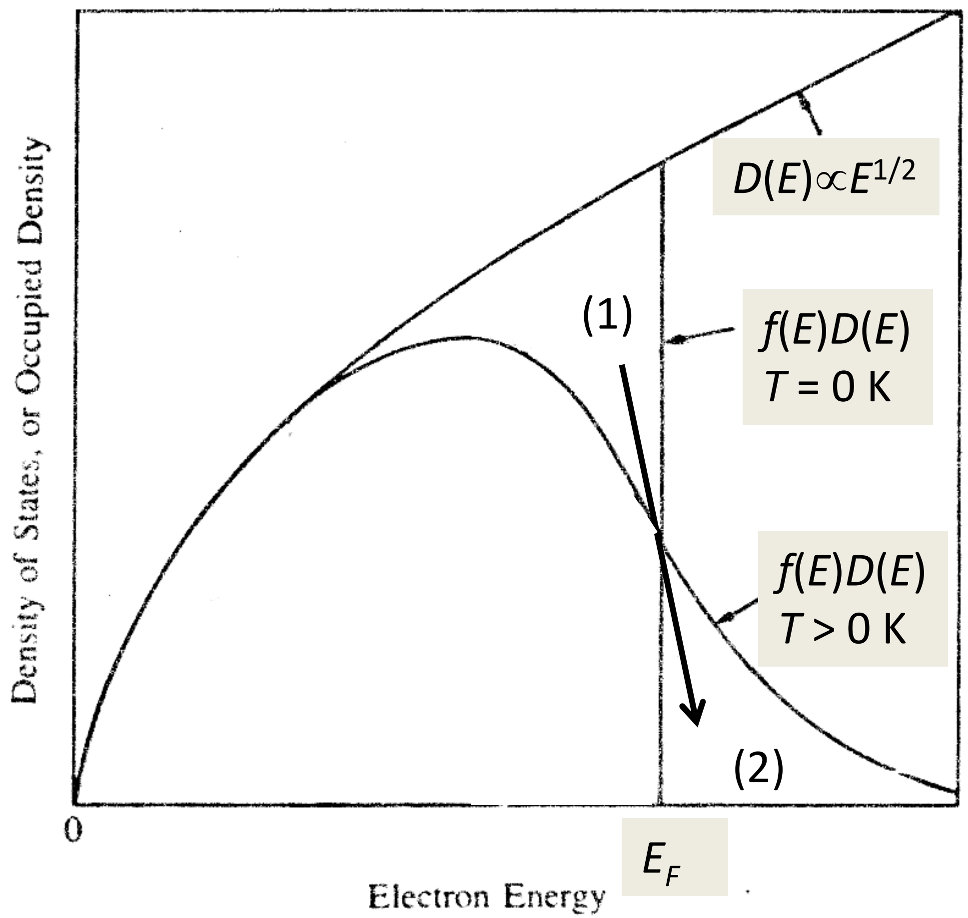
$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \qquad (11.19)$$

$$= \frac{3}{2}\frac{N}{E} \qquad (11.20)$$

- The number of orbits per unit range of energy at the Fermi surface is

$$D(E_F) \propto \frac{N}{E_F}$$

where *N* is the total conduction electrons



- For $T = 0$ K, area with $E < E_F$ represents filled orbits (states)
- For $T > 0$ K, area under the curve represents filled orbits (states)

Heat capacity

- The question that caused the greatest difficulty in the early development of the electron theory of metals concerns the heat capacity of the conduction electrons.
- Classical statistical mechanics predicts that a free particle should have a heat capacity of $3/2k_B$, where k_B is the Boltzmann constant.
- If N atoms each give one valence electron to the electron gas, and the electrons are freely mobile, then the electronic contribution to the heat capacity should be $3/2Nk_B$, just as for the atoms of a monatomic gas.
- But the observed electronic contribution at room temperature is usually less than 0.01 of this value.

- This discrepancy was resolved only upon the discovery of the Pauli exclusion principle and the Fermi distribution function.
- When we heat the specimen from absolute zero not every electron gains an energy ~$k_B T$ as expected classically, but only those electrons, which have the energy within an energy range $k_B T$ of the Fermi level, can be excited thermally.
- These electrons gain an energy, which is itself of the order of $k_B T$.
- This gives a qualitative solution to the problem of the heat capacity of the conduction electron gas.
- If N is the total number of electrons, only a fraction of the order of $k_B T/E_F$ can be excited thermally at temperature T, because

- Each of these Nk_BT/E_F electrons has a thermal energy of the order of k_BT.
- The total electronic thermal kinetic energy U is of the order of $U \approx (Nk_BT/E_F)k_BT$.
- The electronic heat capacity is $C_{el} = dU/dT \approx Nk_B(k_BT/E_F)$ and is directly proportional to T, in agreement with the experimental results.
- At room temperature C is smaller than the classical value $\approx Nk_B$ by a factor 0.01 or less.
- We now derive a quantitative expression for the electronic heat capacity valid at low temperatures $k_BT << E_F$

11.8 Specific heat, C_{el}, for electron gas

- The total energy of a system of N electrons at temperature T is

$$U = \int_0^\infty \underbrace{E\underbrace{D(E)\,f(E)}_{\text{density}}}_{\text{number}} dE \qquad (11.21)$$

$$= \int_0^\infty E\,\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\,\frac{1}{exp\left(\frac{E-E_F}{k_B T}\right)+1}\,dE$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \underbrace{\int_0^\infty \frac{E^{3/2}\,dE}{1+exp\left(\frac{E-E_F}{k_B T}\right)}}_{\text{Fermi-Dirac integral}} \qquad (11.22)$$

- The Fermi-Dirac integral can be written as

$$F_j(y_0) = \int_0^\infty \frac{y^j dy}{1 + exp(y - y_0)} \qquad (11.23)$$

- For y_0 large and positive

$$F_j(y_0) \approx \frac{y_0^{j+1}}{(j+1)}\left[1 + \frac{\pi^2 j(j+1)}{6y_0^2} + \cdots\right] \quad y_0 >> 1$$

- Now back to Eq. (11.22), let $y = \frac{E}{k_B T}$, then

$$dy = \frac{dE}{k_B T}$$

- Also $y_0 = \dfrac{E_F}{k_B T}$, and for large y_0, $E_F >> k_B T$
- $j = 3/2$
- Then

$$\int_0^{\infty} \frac{(yk_BT)^{3/2} dy k_B T}{1 + exp(y - y_0)}$$

$$= (k_BT)^{5/2} \int_0^{\infty} \frac{y^{3/2} dy}{1 + exp(y - y_0)}$$

$$= (k_BT)^{5/2} F_{3/2}\underbrace{\left(\frac{E_F}{k_BT}\right)}_{y_0}$$

$$\approx (k_BT)^{5/2} \times \frac{\left(\frac{E_F}{k_BT}\right)^{5/2}}{\left(\frac{5}{2}\right)} \left[1 + \frac{\pi^2 \left(\frac{3}{2}\right)\left(\frac{5}{2}\right)}{6\left(\frac{E_F}{k_BT}\right)^2} + \cdots\right]$$

$$\approx \frac{2}{5} E_F^{5/2} \left[1 + \frac{5}{8}\left(\frac{\pi k_B T}{E_F}\right)^2\right] \qquad E_F >> k_BT \qquad (11.24)$$

- Therefore the energy is

$$U \approx \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \times \frac{2}{5} E_F^{5/2} \left[1 + \frac{5}{8}\left(\frac{\pi k_B T}{E_F}\right)^2\right] \qquad (11.25)$$

- For $T > 0$ K, the Fermi energy is

$$E_F \approx E_{F0}\left[1-\frac{(\pi k_B T)^2}{12E_{F0}^2}\right] \qquad (11.26)$$

where E_{F0} is the energy at $T = 0$ K

- So the energy becomes

$$U \approx \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left\{\frac{2}{5}E_{F0}^{5/2}\left[1-\frac{5}{24}\left(\frac{\pi k_B T}{E_F}\right)^2\right]\times\left[1+\frac{5}{8}\left(\frac{\pi k_B T}{E_F}\right)^2\right]\right\}$$

$$U \approx \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\times\frac{2}{5}E_{F0}^{5/2}\left[1+\frac{5}{12}\left(\frac{\pi k_B T}{E_F}\right)^2\right]$$

$$U \approx \frac{VE_{F0}^{5/2}}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[1+\frac{5}{12}\left(\frac{\pi k_B T}{E_F}\right)^2\right] \qquad (11.27)$$

- But

$$N = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

- Therefore

$$U = \frac{3}{5}NE_{F0} + \frac{N\pi^2 k_B^2 T^2}{4E_F}$$

$$U(T) = U_0(T=0) + \frac{N\pi^2 k_B^2 T^2}{4E_F} \qquad (11.28)$$

- Therefore

$$\boxed{C_{el} = \left(\frac{\partial U}{\partial T}\right)_{V,el} = \frac{N\pi^2 k_B^2 T}{2E_F}} \qquad (11.29)$$

- Compare with

$$C_{el(classic)} = \frac{3}{2} N k_B$$

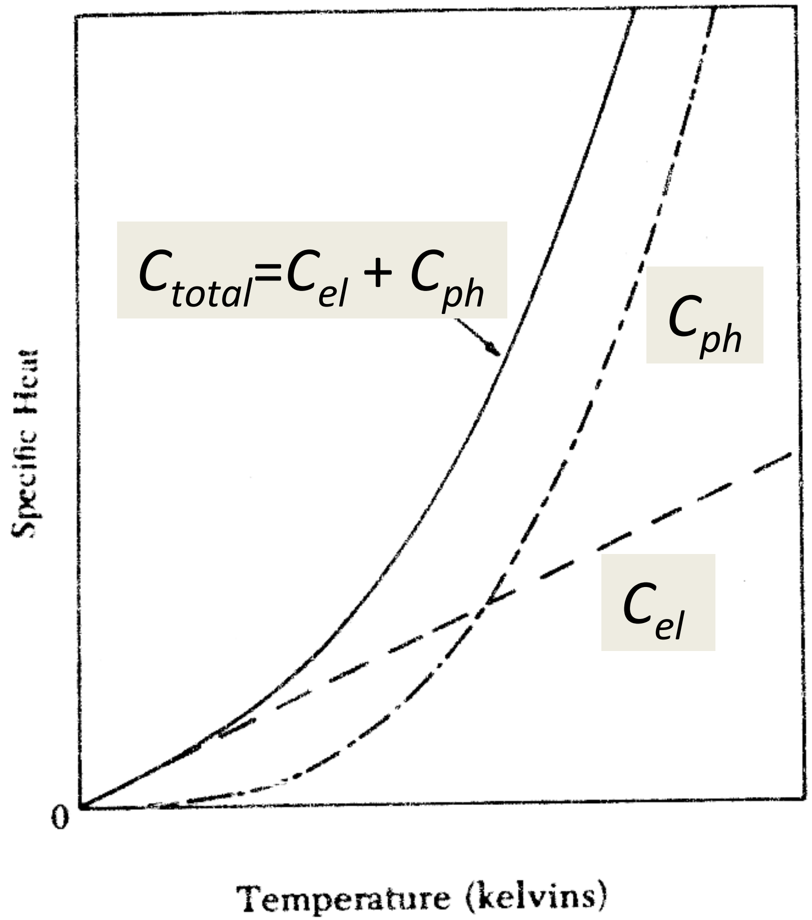
- Therefore

$$C_{el(quantum)} = \frac{\pi^2 k_B T}{3 E_F} \times C_{el(classic)}$$

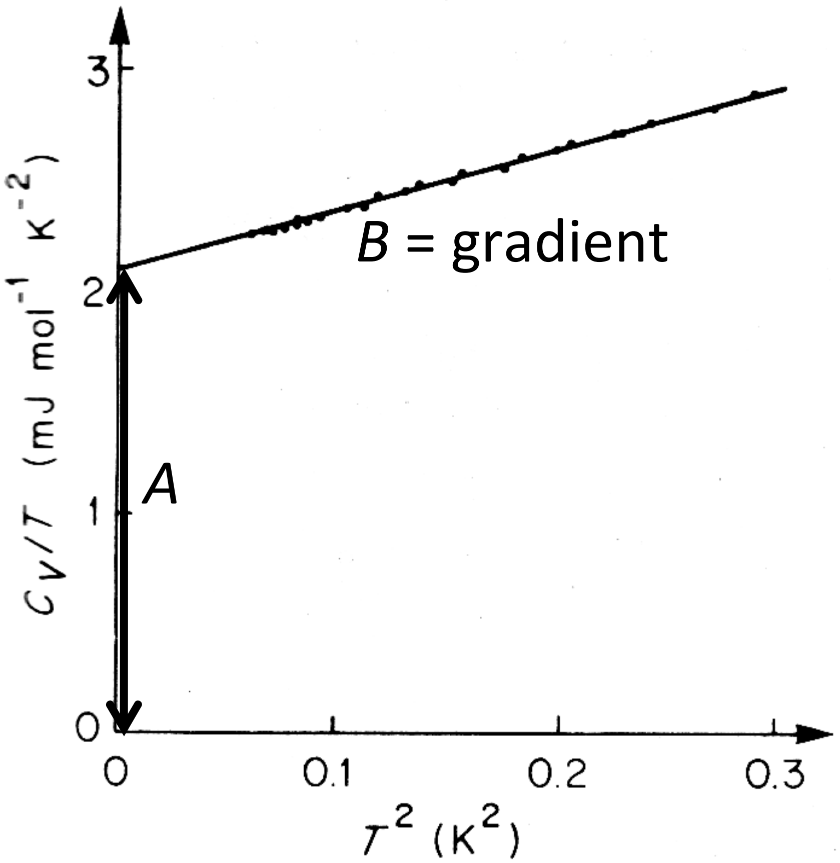
- The total specific heat for a metal is

$$C_{total(metal)} = C_{electron} + C_{phonon}$$

$$C_{total(metal)} = AT + BT^3$$



C_{total}=C_{el} + C_{ph}
C_{ph}
C_{el}
Specific Heat
0
Temperature (kelvins)



B = gradient
A
C_V/T (mJ mol^{-1} K^{-2})
0
1
2
3
0
0.1
0.2
0.3
T^2 (K^2)

11.9 Electrical conductivity, σ, and Ohm law

- The momentum of a free electron is related to its wave vector by

  $$\boldsymbol{p} = m\boldsymbol{v} = \hbar\boldsymbol{k}$$

- The force acting on an electron of charge $-e$ in an electric field ***E*** and magnetic field ***B*** is

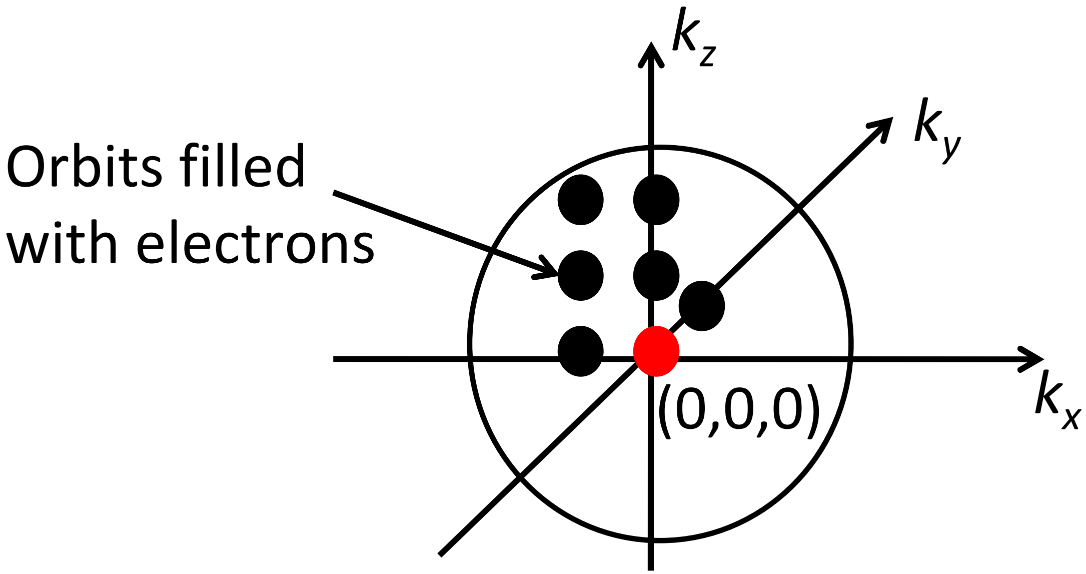
  $$\boldsymbol{F} = m\frac{d\boldsymbol{v}}{dt} = \hbar\frac{d\boldsymbol{k}}{dt} = -e\big(\boldsymbol{E} + (\boldsymbol{v} \times \boldsymbol{B})\big) \qquad (11.30)$$

- If ***B*** = 0 and ***E*** constant, the Fermi sphere in ***k*** space will be displaced at a uniform rate

$$\frac{d\boldsymbol{k}}{dt} = -\frac{e\boldsymbol{E}}{\hbar}$$

$$\boldsymbol{k}(t) - \boldsymbol{k}(0) = -\frac{e\boldsymbol{E}}{\hbar}t \qquad (11.31)$$

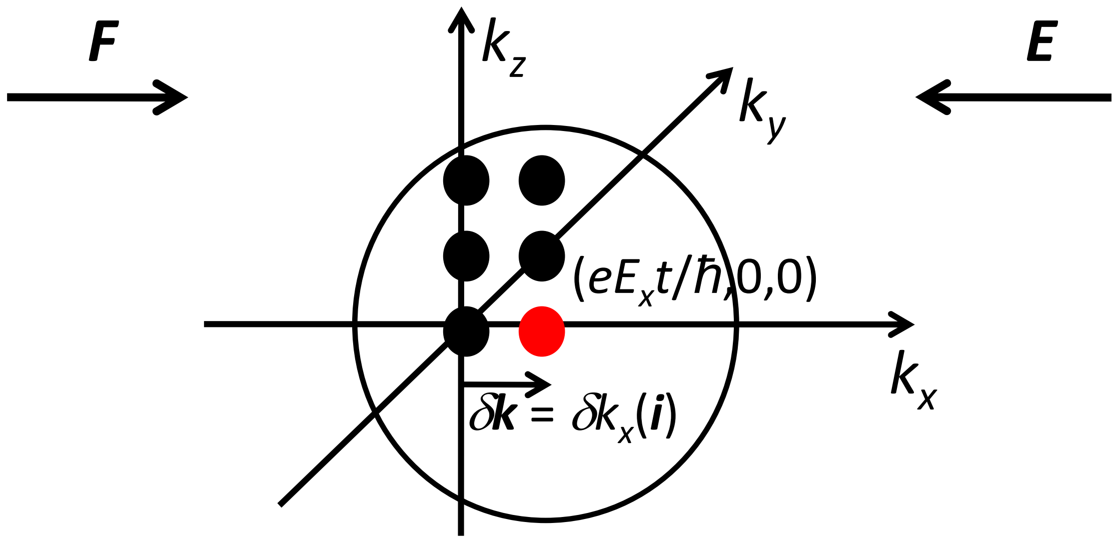
- At temperature T = 0 K (ground state)
- At time t = 0, the center of the Fermi sphere is at $(k_x, k_y, k_z) = (0,0,0)$



- At time $t > 0$, the Fermi sphere is displaced (interacting force acts on the electrons and they moved as a group), with the center of the sphere now at a new position

$$\delta \boldsymbol{k} = -\frac{e\boldsymbol{E}t}{\hbar} \tag{11.32}$$

- The negative sign indicates that the direction of the displacement $\delta\boldsymbol{k}$ is opposite to the direction of $\boldsymbol{E}$
- If $\boldsymbol{E} = E_x(-\hat{\boldsymbol{\imath}})$, then $\boldsymbol{F} = F_x(\hat{\boldsymbol{\imath}})$ and $\delta\boldsymbol{k} = \delta k_x(\hat{\boldsymbol{\imath}})$



- Due to collisions of electrons with impurities, lattice imperfections and phonons, the Fermi sphere can be stationary in an electric field
- If τ is the collision time, then the displacement is

$$\delta \boldsymbol{k} = -\frac{e\boldsymbol{E}\tau}{\hbar} \qquad (11.33)$$

- Therefore the drift velocity is

$$\boldsymbol{v} = -\frac{e\boldsymbol{E}\tau}{m} \qquad (11.34)$$

- If ***E*** is constant and there are *n* electrons of charge $q = -e$ per unit volume, then the electric current density is

$$\boldsymbol{j} = nq\boldsymbol{v} = -ne\boldsymbol{v} = \frac{ne^2\tau\boldsymbol{E}}{m} \quad \text{(Ohm law)} \quad (11.35)$$

- The electrical conductivity σ is define as $\boldsymbol{j} = \sigma\boldsymbol{E}$
- Thus

$$\sigma = \frac{ne^2\tau}{m} \qquad (11.36)$$

- The electrical resistivity ρ is define as the reciprocal of electrical conductivity σ, thus

$$\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau} \tag{11.37}$$

- For pure Cu

- Ratio of conductivities

$$\frac{\sigma(4\ \mathrm{K})}{\sigma(300\ \mathrm{K})} \approx 10^5$$ $\sigma\uparrow$ when $T\downarrow$ because $\rho\downarrow$

- Ratio of mean free path

$$\frac{\ell(4\ \mathrm{K})}{\ell(300\ \mathrm{K})} \approx \frac{0.3\ \mathrm{cm}}{3\times10^{-6}\ \mathrm{cm}} \approx 10^5$$

$\ell\uparrow$ when $T\downarrow$ because of less collisions

11.10 Matthiessen's rule

- The electrical resistivity at temperature *T* is

$$\rho = \rho_i + \rho_L \qquad (11.38)$$

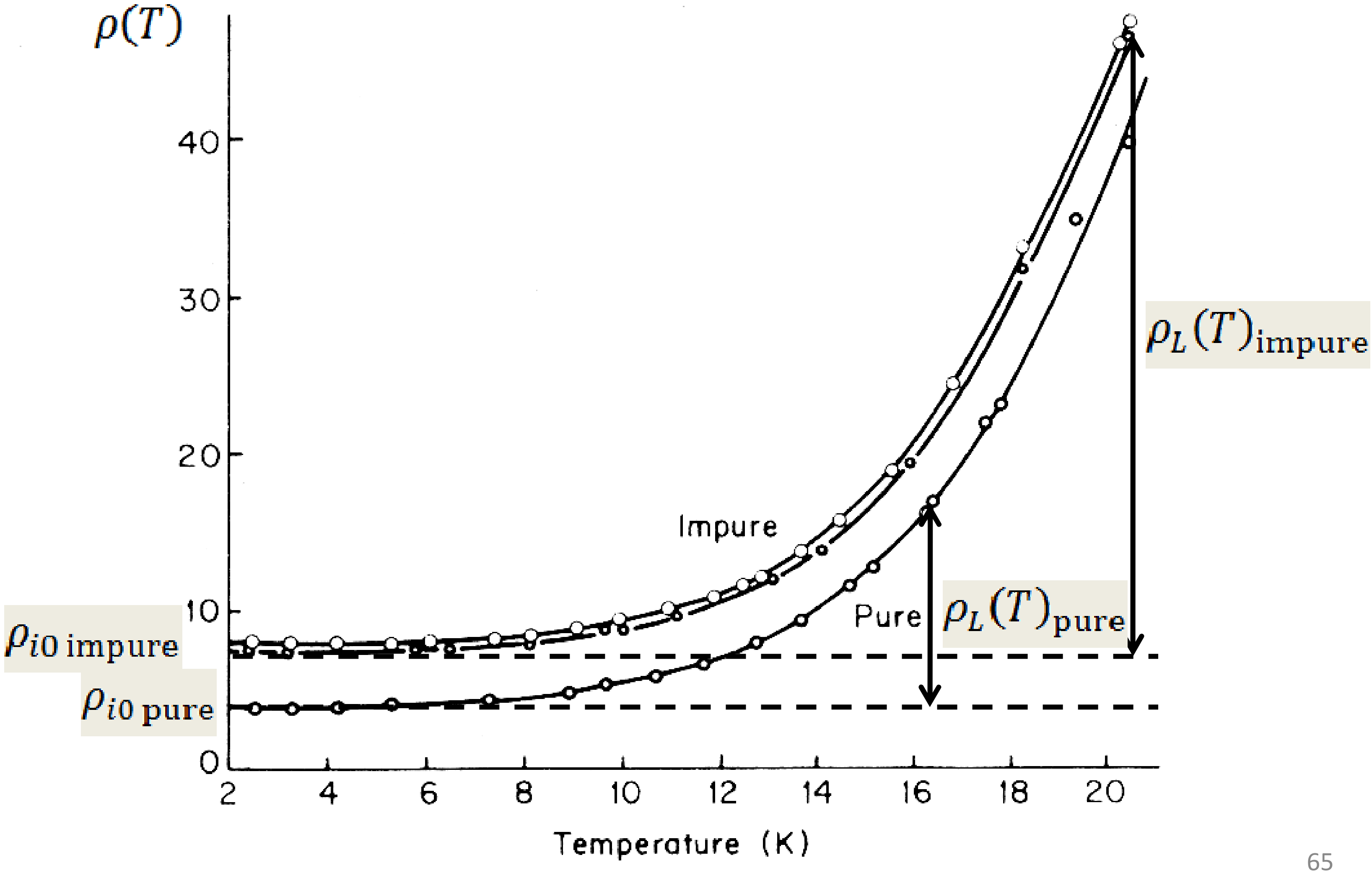
- ρ_L is the resistivity due to the collisions of conduction electrons with phonons, thus dependent on temperature
- ρ_i is the resistivity due to the collisions of conduction electrons with impurities and lattice imperfections, thus dependent on the purity of metals
- When temperature T → 0,

  $\rho_L \rightarrow 0$ and

  $\rho \rightarrow \rho_{i0} \propto$ purity (a constant value)

- Thus

$$\rho(T) = \rho_{i0} + \rho_L(T) \qquad (11.39)$$



11.11 Electron motion in magnetic field *B*

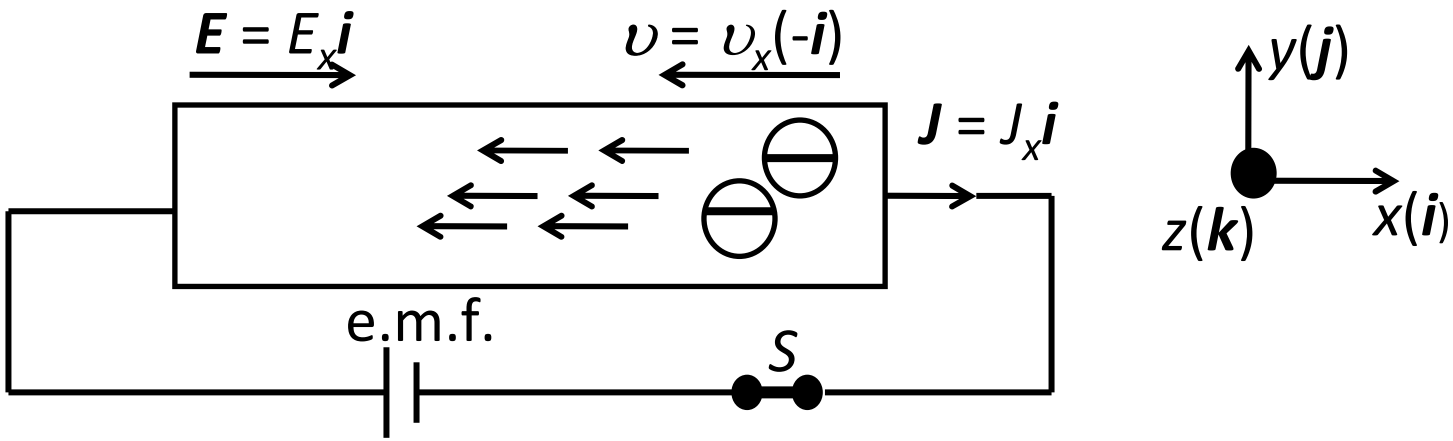
- Please write short notes on cyclotron frequency

$$\omega_c = \frac{eB}{m}$$

11.12 Hall effect and Hall electric field

- Hall electric field is produced by positive charges and negative charges at two surfaces of a conductor placed in a magnetic field
- Consider a bar conductor connected to an electrical circuit
- When switch *S* is close, an electric current ***J*** flows in the positive *x* direction inside the bar

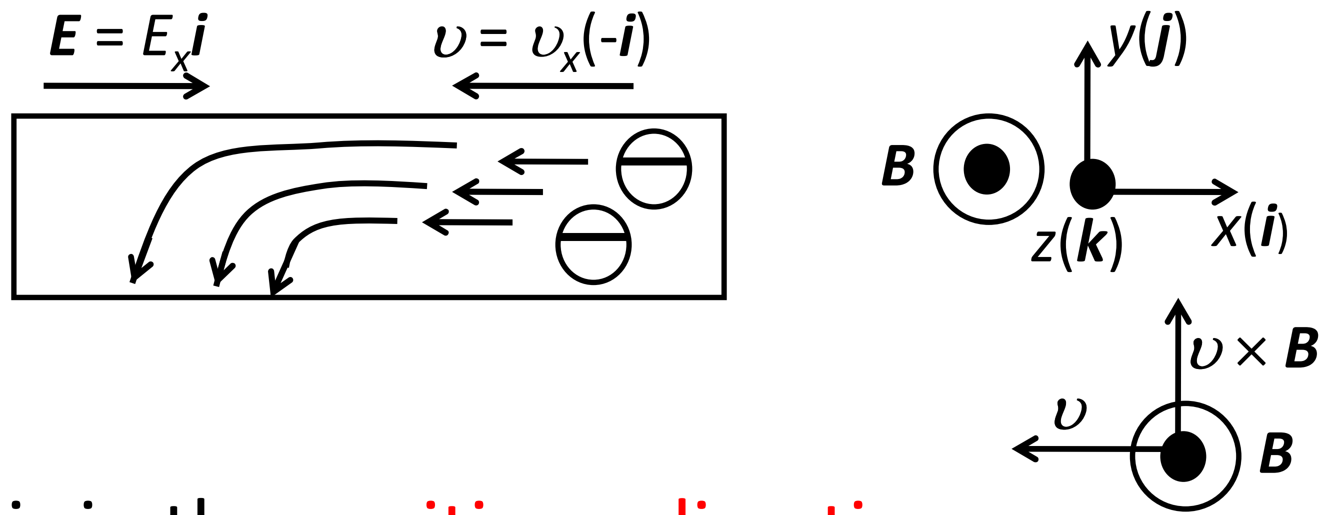
- This means that conduction electrons move with velocity υ in the negative x direction



- When a magnetic field $\boldsymbol{B}$ (in the z direction) is introduced, a Lorentz force

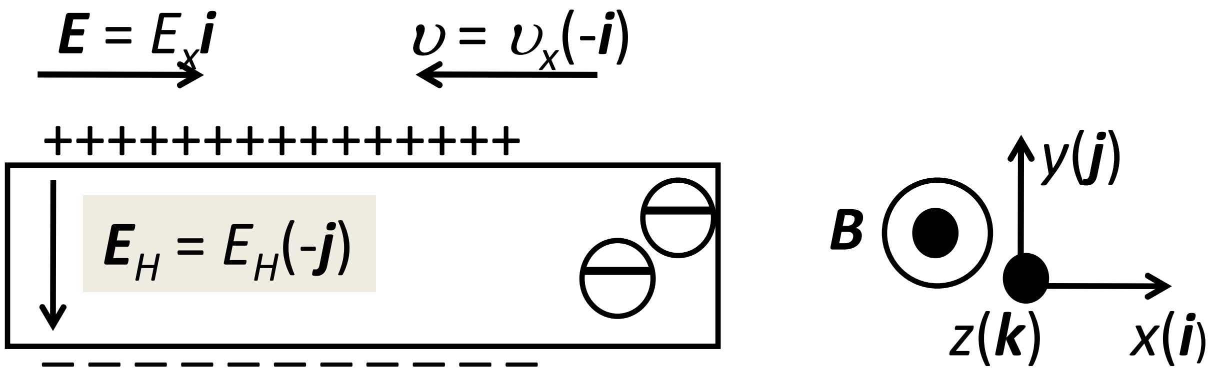
$$\boldsymbol{F}_L = -e(\boldsymbol{\upsilon} \times \boldsymbol{B})$$

acts on the electrons that force their motion to bend downwards (negative y direction)



- $(\boldsymbol{\upsilon} \times \boldsymbol{B})$ is in the positive *y* direction
- Thus for electrons, $\boldsymbol{F}_L = -e(\boldsymbol{\upsilon} \times \boldsymbol{B})$, the Lorentz force is in the negative *y* direction
- This causes electrons to be accumulated at the bottom surface of the bar, thus negatively charged
- The top surface of the bar is positively charged (lacked of electrons)

- These positive and negative charges produce an electric field in the negative y direction called the Hall electric field $\boldsymbol{E}_H = E_H(-\hat{\boldsymbol{j}})$



- Note that $\boldsymbol{E}_H \perp \boldsymbol{\upsilon}$ and $\boldsymbol{B}$
- The Lorentz force

$$\boldsymbol{F}_L = -e(\boldsymbol{\upsilon} \times \boldsymbol{B})$$

$$\boldsymbol{F}_L = e\upsilon_x B(-\hat{\boldsymbol{j}}) \ \downarrow \qquad (11.40)$$

- The Hall electric field creates a Hall force on the electrons to counter the Lorentz force so that the system is in the steady state

$$\boldsymbol{F}_H = -e\boldsymbol{E}_H$$

$$\boldsymbol{F}_H = -eE_H(-\hat{\boldsymbol{j}})$$

$$\boldsymbol{F}_H = eE_H(\hat{\boldsymbol{j}}) \uparrow \quad (11.41)$$

- In the steady state

$$|\boldsymbol{F}_L| = |\boldsymbol{F}_H|$$

$$ev_xB = eE_H$$

- Therefore the Hall electric field is

$$E_H = v_xB \quad (11.42)$$

- The electric current density is

$$J_x = n(-e)v_x = -nev_x$$

- Therefore

$$v_x = -J_x/ne \qquad (11.43)$$

- Substituting Eq. (11.43) into Eq. (11.42)

$$E_H = -\frac{1}{ne}J_x B \qquad (11.44)$$

- The Hall constant is

$$R_H = \frac{E_H}{J_x B} = -\frac{1}{ne} \qquad (11.45)$$

- R_H has units of volt m^3 amp^{-1} weber^{-1}

- Some values for Hall constant at room temperature
- – for electrons
- + for holes

Conductor	Hall Constant
Li	-1.7×10^{-10}
Na	-2.50
Cu	-0.55
Ag	-0.84
Au	-0.72
Zn	$+0.30$
Cd	$+0.60$
Al	-0.30

11.13 Thermal conductivity for metals

- The electrons thermal conductivity is

$$K_{el} = \frac{1}{3} C_V \upsilon \ell$$

where C_V is the specific heat per unit volume for electrons, υ is the mean velocity of electrons and ℓ is mean free path of electrons

- From Eq. (11.29)

$$C_{el} = \frac{N\pi^2 k_B^2 T}{2E_F V} = C_V$$

$$\boxed{C_{el} = \left(\frac{\partial U}{\partial T}\right)_{V,el} = \frac{N\pi^2 k_B^2 T}{2E_F}}$$

- Thus

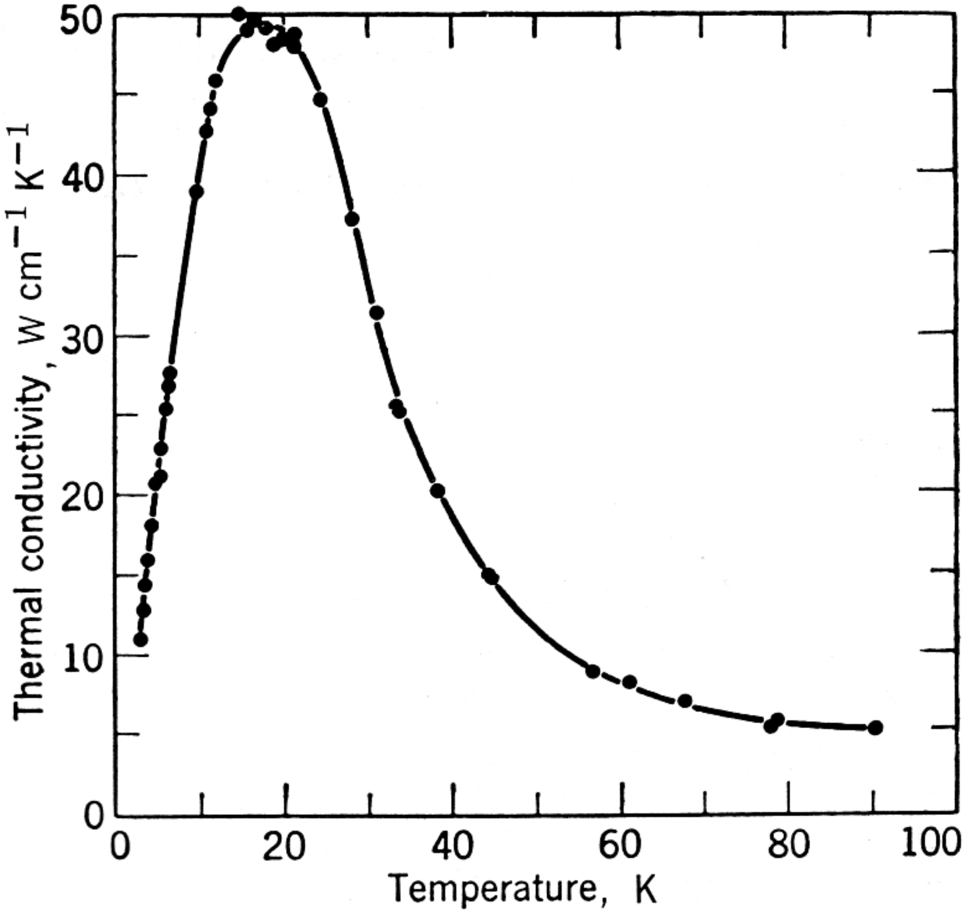
$$K_{el} = \frac{1}{3}\frac{\pi^2 k_B^2 T n}{2E_F} \upsilon \ell$$

- Substituting for $E_F = \frac{1}{2} m\upsilon_F^2$
- Then

$$K_{el} = \frac{\pi^2 k_B^2 T n}{3m\upsilon_F^2} \cdot \upsilon_F \cdot \ell = \frac{\pi^2 n k_B^2 T \tau}{3m} \qquad (11.46)$$

where $\tau = \frac{\ell}{\upsilon_F}$ is the collision time

- Typical graph of K_{el} for Cu
- K_{el} is maximum at temperature around 15 K



- For pure metals $K_{electrons} > K_{phonons}$ at all temperatures

11.14 Wiedemann-Franz law

- This law says that for metals at temperatures that are not too low, the ratio of thermal conductivity and electrical conductivity for electron gas is directly proportional to the temperature

$$\frac{K}{\sigma} \propto T = LT$$

where L is a proportional constant independent of the type of metals

- Substitute K_{el} for K, and $\tau_{\text{thermal}} = \tau_{\text{electrical}} = \tau$

$$\frac{K}{\sigma} = \frac{\pi^2 n k_B^2 T \tau}{3m} \Big/ \frac{ne^2\tau}{m}$$

$$\frac{K}{\sigma} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T \qquad (11.47)$$

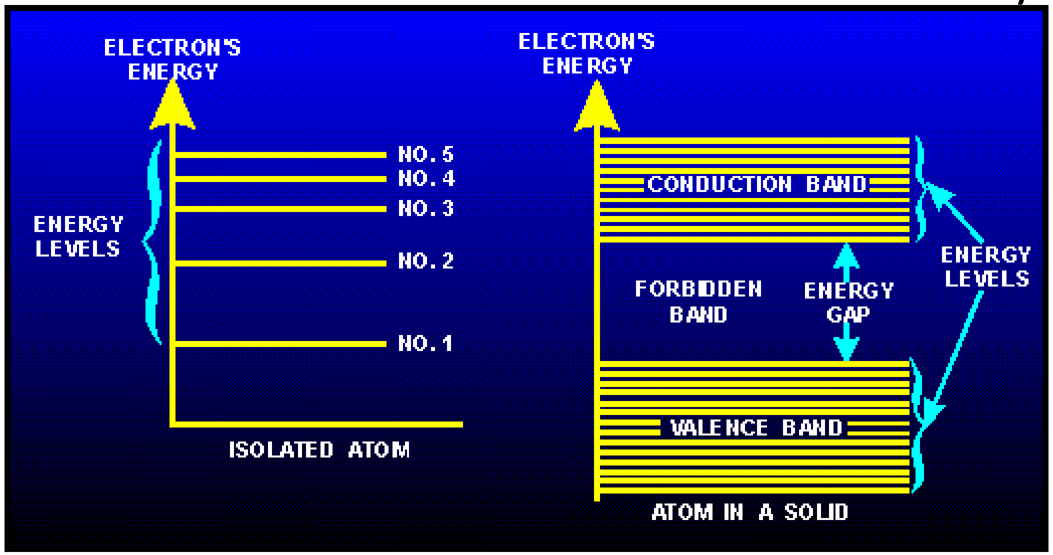
- Therefore the proportional constant *L* or the Lorentz number *L* is

$$L = \frac{K}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \qquad (11.48)$$

$$\approx 2.45 \times 10^{-8}\ \mathrm{W\Omega K^{-2}}$$

Why We Study Energy Bands?

- The free electron model gives us a good insight into many properties of metals, such as the heat capacity, thermal conductivity and electrical conductivity.
- However, this model fails to help us other important properties.
  - For example, it does not predict the difference between metals, semiconductors and insulators. It does not explain the occurrence of positive values of the Hall coefficient.
  - Also the relation between conduction electrons in the metal and the number of valence electrons in free atoms is not always correct.



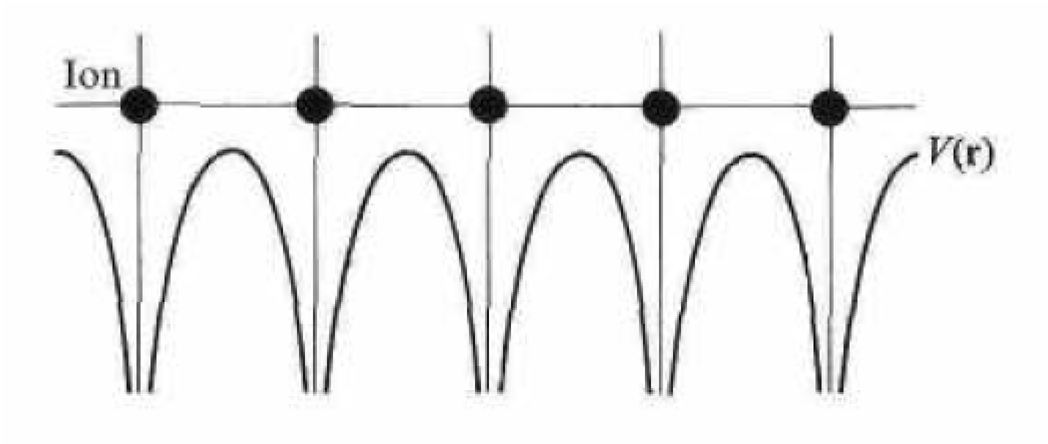
- A more accurate theory is needed to answer these questions.
- The problem of electrons in a solid is in general a many-electron problem.
- The full Hamiltoniam of the solid contains not only the one-electron potentials describing the interactions of the electrons with atomic nuclei, but also pair potentials describing the electron-electron interactions.
- The many-electron problem is impossible to solve exactly and therefore we need simplified assumptions.
- The simplest approach we have already considered, it is a free electron model.
- The next step in building the complexity is to consider an independent electron approximation, assuming that all the interactions are described by an effective potential.

- One of the most important properties of this potential is that it is periodic on a lattice

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{T})$$

where **T** is a lattice vector.

- Qualitatively, a typical crystalline potential might be expected to have a form shown in figure below, resembling the individual atomic potentials as the ion is approached closely and flattening off in the region between ions.



The crystal potential seen by the electron

12 Energy Bands

12.1 Free electron model

- The 3-dimensional quantized free electron gas model with Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2}\psi_{\boldsymbol{k}}(\boldsymbol{r}) = E_{\boldsymbol{k}}\psi_{\boldsymbol{k}}(\boldsymbol{r}) \qquad (V(r) = 0)$$

shows that the equation for the allowed electron energy is

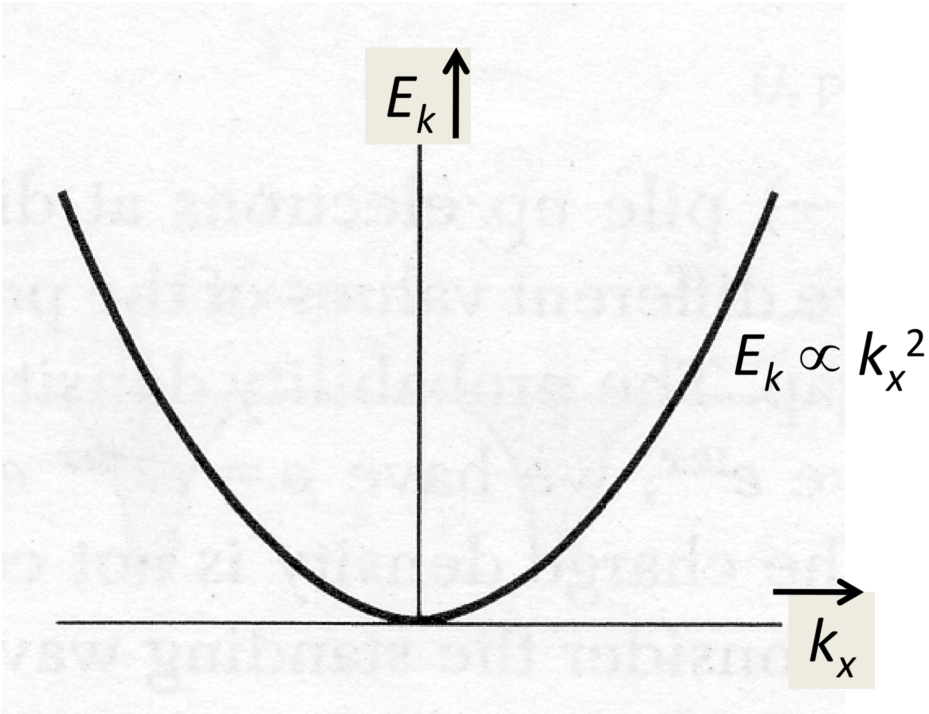
$$E_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$k_x, k_y, k_z = \pm n\frac{2\pi}{L} \qquad \mathrm{n} = \mathrm{integer}$$

- $\psi_{\boldsymbol{k}}(\boldsymbol{r})$ is the electron wave function

  $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = exp(i\boldsymbol{k} \cdot \boldsymbol{r})$

- A plot of *E* versus k_x (energy band structure in *x* direction) produces a parabola



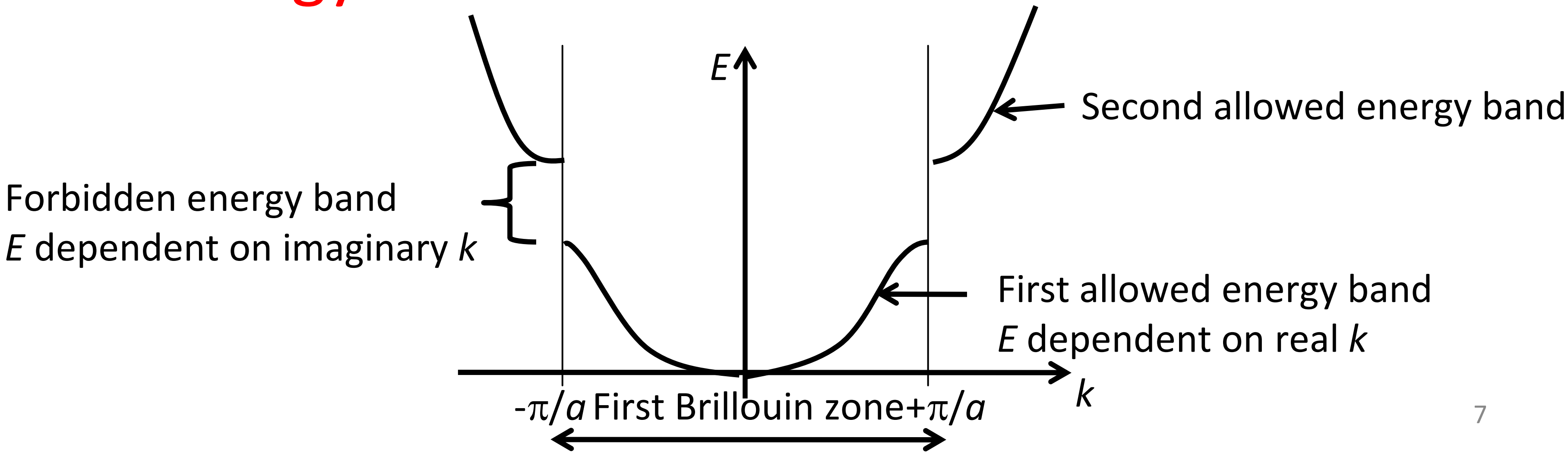
$(k_y, k_z = 0)$

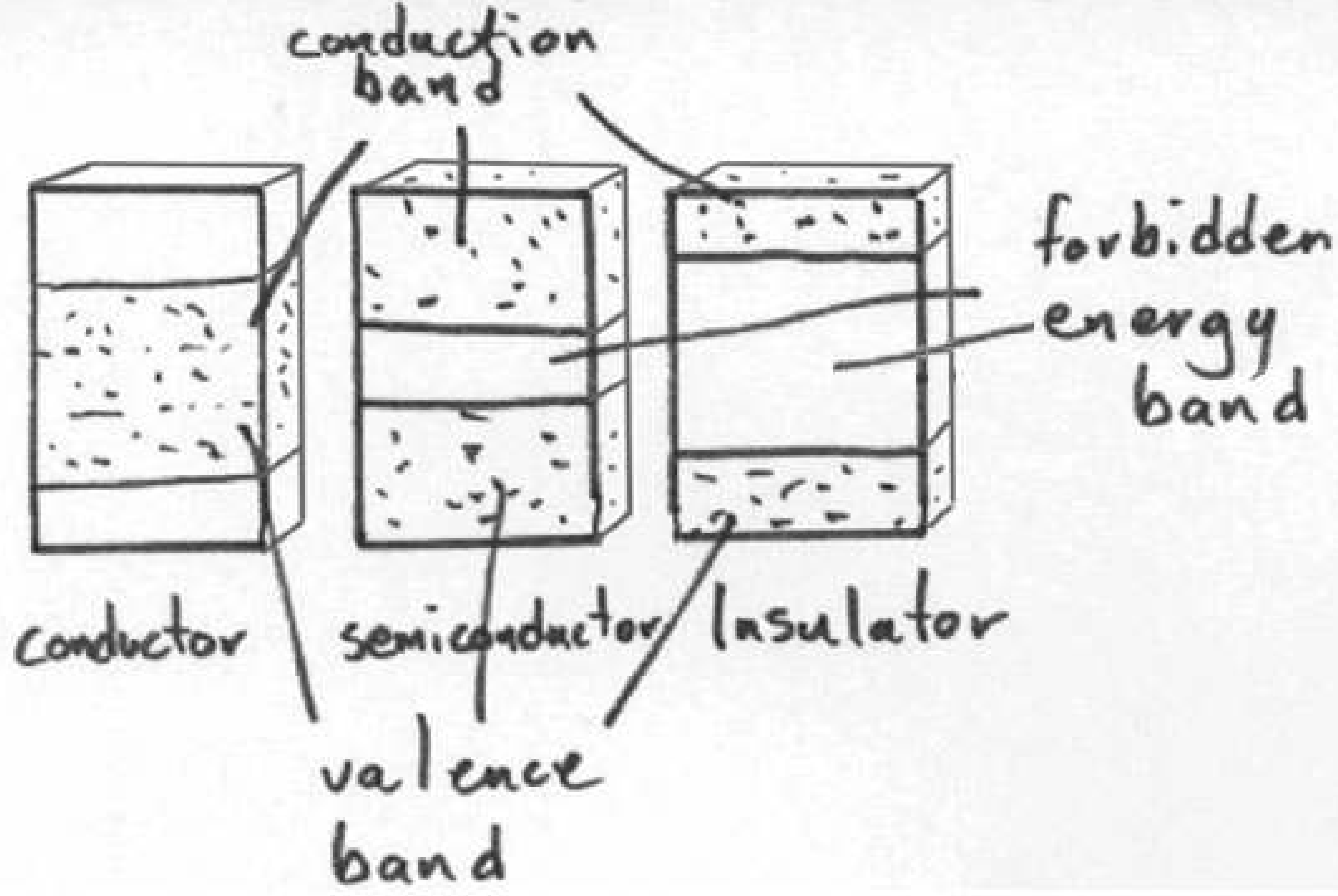
12.2 Nearly free electron model

- Electrons in real crystals experience small perturbations due to the periodic potential $V(r)$ of ion cores
- Thus electrons are no longer free
- Their energy band structure can be explained by quantized nearly free electron model with Schrödinger equation

$$\underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2}}_{\text{Kinetic energy}}\psi_{\boldsymbol{k}}(\boldsymbol{r}) + \underbrace{V(r)}_{\text{Potential energy}}\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \underbrace{E_{\boldsymbol{k}}}_{\text{Total energy}}\psi_{\boldsymbol{k}}(\boldsymbol{r}) \qquad (12.1)$$

- $\psi_{\boldsymbol{k}}(\boldsymbol{r})$ and $E_{\boldsymbol{k}}$ are the wave functions and energy of the electrons
- The $V(r)$ term for the periodic potential causes only certain electron energies $E_{\boldsymbol{k}}$ to be allowed, thus there exist forbidden $E_{\boldsymbol{k}}$
- For a linear monoatomic lattice with lattice constant *a* and periodic potential, the shape of its energy band structure is





conduction band
forbidden energy band
conductor
semiconductor
Insulator
valence band

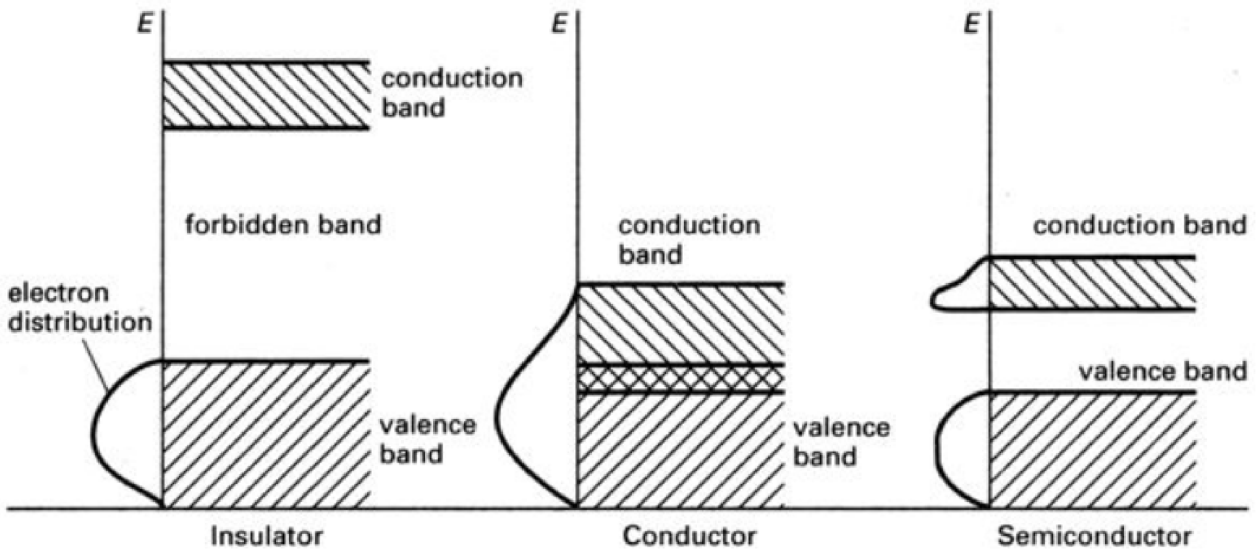
Oxford Dictionary

energy bands

- A range of energies that electrons can have in a solid.
- In a single atom, electrons exist in discrete energy levels.
- In a crystal, in which large numbers of atoms are held closely together in a lattice, electrons are influenced by a number of adjacent nuclei and the sharply defined levels of the atoms become bands of allowed energy; this approach to energy levels in solids is often known as the **band theory**.
- Each band represents a large number of allowed quantum states.
- Between the bands are **forbidden bands**.
- The outermost electrons of the atoms (i.e. the ones responsible for chemical bonding) form the **valence band** of the solid.
- This is the band, of those occupied, that has the highest energy.

- The band structure of solids accounts for their electrical properties.
- In order to move through the solid, the electrons have to change from one quantum state to another.
- This can only occur if there are empty quantum states with the same energy.
- In general, if the valence band is full, electrons cannot change to new quantum states in the same band.
- For conduction to occur, the electrons have to be in an unfilled band – the **conduction band**.
- Metals are good conductors either because the valence band and the conduction band are only half-filled or because the conduction band overlaps with the valence band; in either case vacant states are available.
- In insulators the conduction band and valence band are separated by a wide forbidden band and electrons do not have enough energy to 'jump' from one to the other.

- In intrinsic semiconductors the forbidden gap is narrow and, at normal temperatures, electrons at the top of the valence band can move by thermal agitation into the conduction band (at absolute zero, a semiconductor would act as an insulator).
- Doped semiconductors have extra bands in the forbidden gap.



Energy bands

12.3 Bloch function

- Bloch theorem states that the solution for the Schrödinger equation of Eq. (12.1) is a wave function of the form

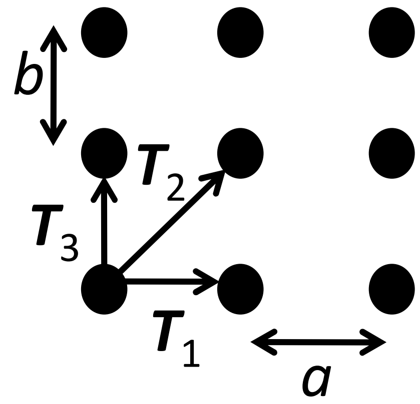
$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = u_{\boldsymbol{k}}(\boldsymbol{r})exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \qquad (12.2)$$

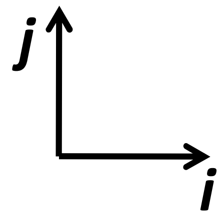
- This equation is called the Bloch function which is a progressive wave equation
- $u_{\boldsymbol{k}}(\boldsymbol{r})$ is a periodic function where its period is the same as the lattice period
- $u_{\boldsymbol{k}}(\boldsymbol{r})$ exist because of $V(r)$ which has the same period
- Subscript ***k*** indicates that $u_{\boldsymbol{k}}(\boldsymbol{r})$ is dependent on wave vector ***k***

$$u_{\boldsymbol{k}}(\boldsymbol{r}) = u_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{T}) \qquad (12.3)$$

where $\boldsymbol{T}$ is a translational lattice vector

- For 2-dimensional lattice

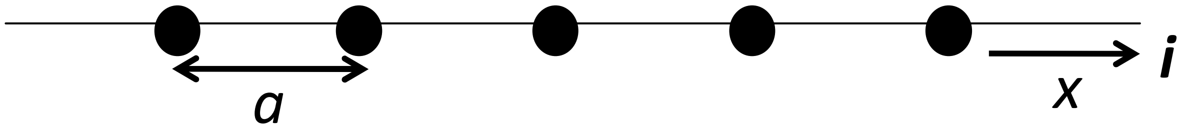




$$\boldsymbol{T} = \boldsymbol{T}_1 \text{ or } \boldsymbol{T}_2 \text{ or } \boldsymbol{T}_3$$

$$\boldsymbol{T} = a\hat{\boldsymbol{\imath}} \text{ or } a\hat{\boldsymbol{\imath}} + b\hat{\boldsymbol{\jmath}} \text{ or } b\hat{\boldsymbol{\jmath}}$$

- For 1-dimensional lattice



- Assuming there are *N* atoms, then from (12.3)

$$u_k(x) = u_k(x+a)$$

$$V(x) = u_k(x) exp(ikx) exp(ika)$$

- The Bloch wave function for $\psi_k(x+a)$ from Eq. (12.2) is

$$\psi_k(x+a) = u_k(x+a) exp\big(ik(x+a)\big)$$

$$= u_k(x) exp(ikx) exp(ika)$$

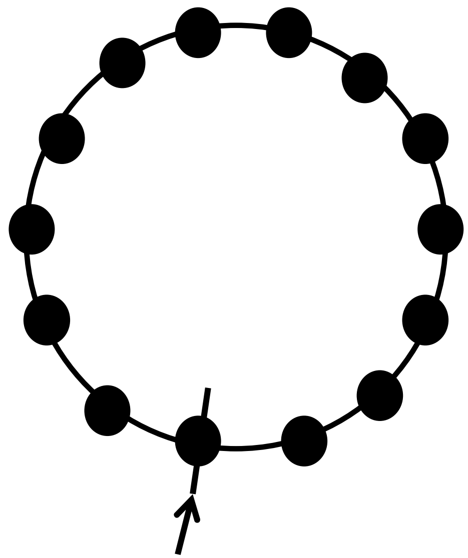
$$= \psi_k(x) C$$

- Where $\psi_k(x) = u_k(x) expikx$ and $C = expika$
- If the monoatomic lattice is made into a circle
- Then the length is *Na* and

  the new period is *Na* and

  $u_k(x) = u_k(x + Na)$

  $V(x) = V(x + Na)$



- The wave function at the point

  where the ends meet is now

$$\psi_k(x + Na) = u_k(x + Na)exp\big(ik(x + Na)\big)$$

$$\equiv \psi_k(x)$$

$$\psi_k(x + Na) = u_k(x) expikx\ expikNa$$
$$= \psi_k(x)C^N$$

- Therefore

$$\psi_k(x) = \psi_k(x)C^N$$
$$C^N = 1$$
$$expikNa = 1 = expin2\pi \tag{12.4}$$

where $n = 0, 1, 2, 3 \ldots N - 1$

- Thus

$$kNa = n2\pi$$
$$k = n\frac{2\pi}{Na}$$

- The Bloch wave function becomes

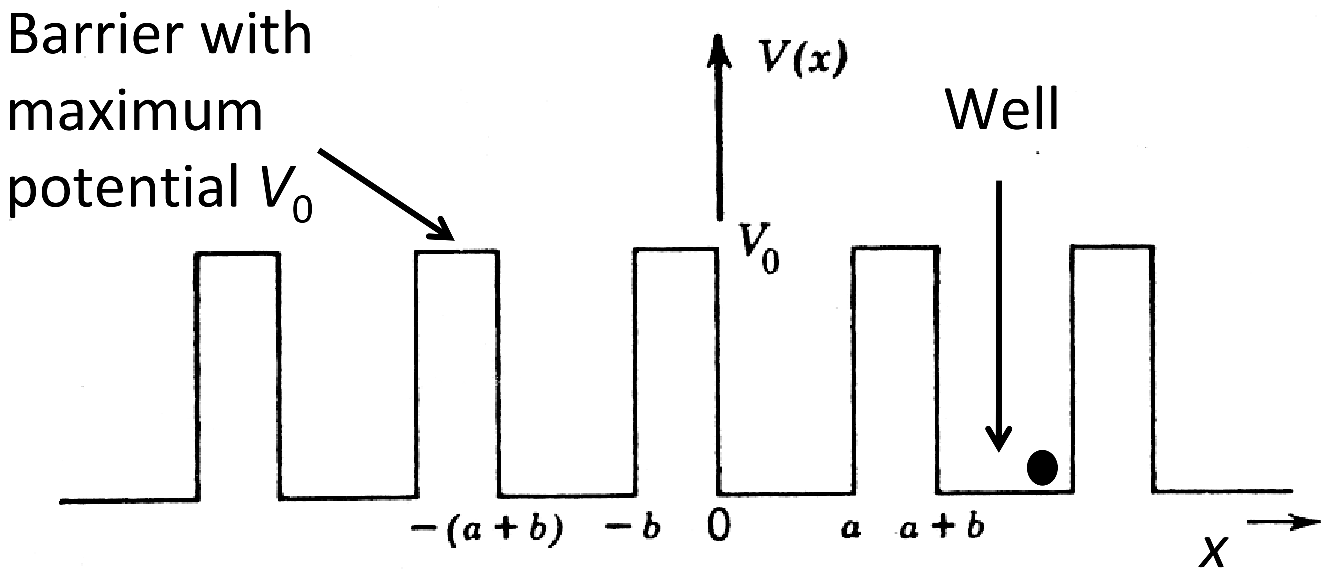
$$\psi_k(x) = u_k(x) exp\left(in\frac{2\pi}{Na}x\right) \quad (12.5)$$

- Substitute this $\psi_k(x)$ into the Schrödinger equation of Eq. (12.1) and the allowed values for $E_{\boldsymbol{k}}$ can be determined provided $V(r)$ is known.

12.4 Kronig-Penney model

- This 1-dimensional model is used to obtain the relationship between *E* and *k* (allowed and forbidden energies) when *V*(*x*) is known

- The periodic potential *V*(*x*) has square wells arrangement such as below



- The Schrödinger equation of Eq. (12.1) for free electrons becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V_0(x)\psi=E\psi \qquad (12.6)$$

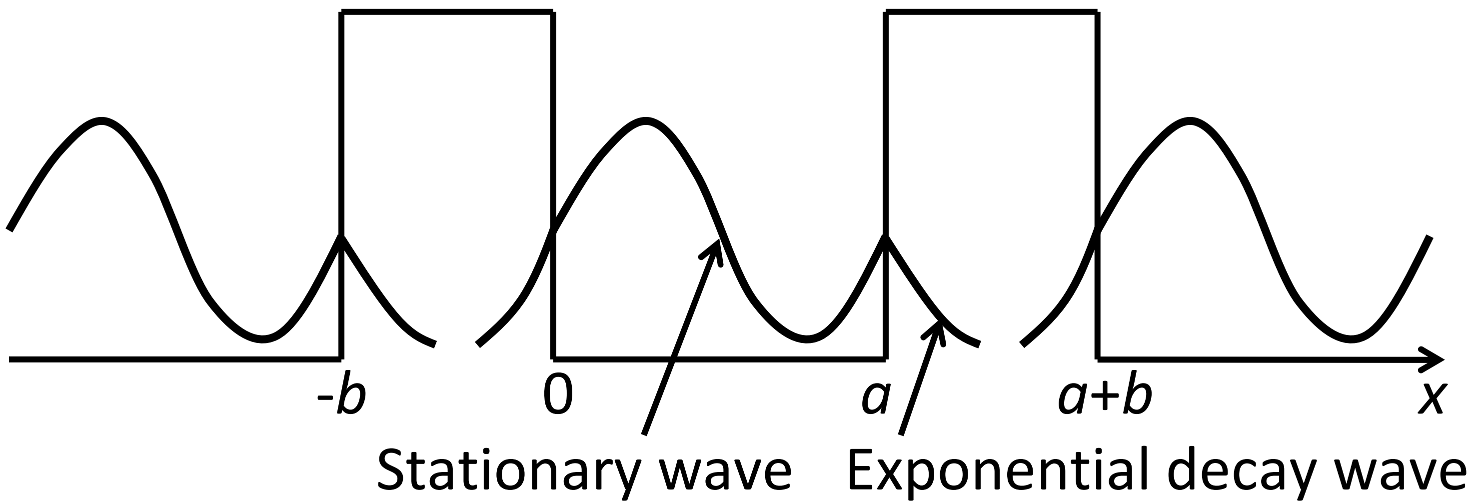
- If V_0 and b are small, the electrons are free to move (free electron gas) and their $E \propto k^2$ (parabola)
- If b is too large and the electron energy $E < V_0$, the probability of tunneling by the electrons through the barriers is zero, and the electrons will be in the wells with quantized energies (values of allowed k given by stationary wave functions in the wells)
- What if b is small and $E < V_0$ ($\rightarrow \infty$)?
- Is there a complete tunneling by the electrons through the barriers?

- In the range $0<x<a$ (inside the well), $V = 0$
- The wave function for Eq. (12.6) is

$$\psi_{well} = Ae^{iKx} + Be^{-iKx} \tag{12.7}$$

- Combination of two progressive plane waves to the right and to the left
- Thus creating a stationary wave
- The energy of the electron is

$$E = \frac{\hbar^2 K^2}{2m} \tag{12.8}$$



- In the range $a<x<a+b$ (inside the barrier), $V = 0$
- The wave function for Eq. (12.6) is

$$\psi_{barrier} = Ce^{Qx} + De^{-Qx} \tag{12.9}$$

- Combination of two exponential decay waves (to the right and to the left) due to tunneling
- The energy of the electron is

$$V_0 - E = \frac{\hbar^2 Q^2}{2m} \qquad (12.10)$$

- The factors *A*, *B*, *C* and *D* are chosen so that ψ and $\partial\psi/\partial x$ are continuous at $x = 0$ and $x = a$
- Condition I

▪ Continuity at $x = 0$

▪ For ψ ,

$$\psi_{well}(0) = \psi_{barrier}(0)$$

$$A + B = C + D \qquad (12.11)$$

▪ For $\partial\psi/\partial x$,

$$\frac{\partial\psi(0)}{\partial x_{well}} = \frac{\partial\psi(0)}{\partial x_{barrier}}$$

$$iKA - iKB = QC - QD \qquad (12.12)$$

- Condition II

- Continuity at $x = a$

- For ψ ,

$$\psi_{well}(a) = \psi_{barrier}(a)$$

$$Ae^{iKa} + Be^{-iKa} = Ce^{Qa} + De^{-Qa} \qquad (12.13)$$

- For $\partial\psi/\partial x$,

$$\frac{\partial\psi(a)}{\partial x_{well}} = \frac{\partial\psi(a)}{\partial x_{barrier}}$$

$$iKAe^{iKa} - iKBe^{-iKa} = QCe^{Qa} - QDe^{-Qa} \quad (12.14)$$

- Condition III

- From Bloch theorem

$$\psi(a) = \psi(-b)e^{ik(a+b)}$$

$$\frac{\partial\psi(a)}{\partial x} = \frac{\partial\psi(-b)}{\partial x}e^{ik(a+b)}$$

where $\psi(a)$ and $\frac{\partial\psi(a)}{\partial x}$ lead $\psi(-b)$ and $\frac{\partial\psi(-b)}{\partial x}$

respectively with phase factor $e^{ik(a+b)}$

- The left side of Eq. (12.13) becomes

$$Ae^{[iKa-ik(a+b)]} + Be^{[-iKa-ik(a+b)]}$$
$$= Ce^{Qa} + De^{-Qa} \qquad (12.13a)$$

- The left side of Eq. (12.14) becomes

$$iKAe^{[iKa-ik(a+b)]} - iKBe^{[-iKa-ik(a+b)]}$$
$$= QCe^{Qa} - QDe^{-Qa} \qquad (12.14a)$$

- The solution for Eqs. (12.11), (12.12), (12.13a) and (12.14a) can be obtained if the determinant of the factors *A*, *B*, *C* and *D* becomes zero
- The solution is

$$\left[\frac{(Q^2 - K^2)}{2QK}\right] \sinh Qb \sin Ka + \cosh Qb \cos Ka$$
$$= \cos k(a+b) \qquad (12.15)$$

- Q is the wave vector in the barrier, K is the wave vector in the well and k is the overall wave vector for the electron
- Consider a high barrier (V_0 large) and narrow ($b \approx 0$) so that bV_0 has a finite value, then

$$\left[\frac{(Q^2 - K^2)}{2QK}\right] Qb \sin Ka + \cos Ka = \cos ka$$

$$\left(\frac{Q^2 b}{2K}\right) \sin Ka - \underbrace{\left(\frac{Kb}{2}\right) \sin Ka}_{\approx 0} + \cos Ka = \cos ka$$

$$\left(\frac{Q^2 b}{2K}\right) \sin Ka + \cos Ka = \cos ka$$

- Define the barrier strength as

$$P = \frac{Q^2 ba}{2} \quad \propto bV_0 \text{ (finite)}$$

- Therefore

$$\left(\frac{P}{Ka}\right)\sin Ka + \cos Ka = \cos ka \qquad (12.16)$$

- If $P \to 0 \quad (V_0 = 0)$, no barrier

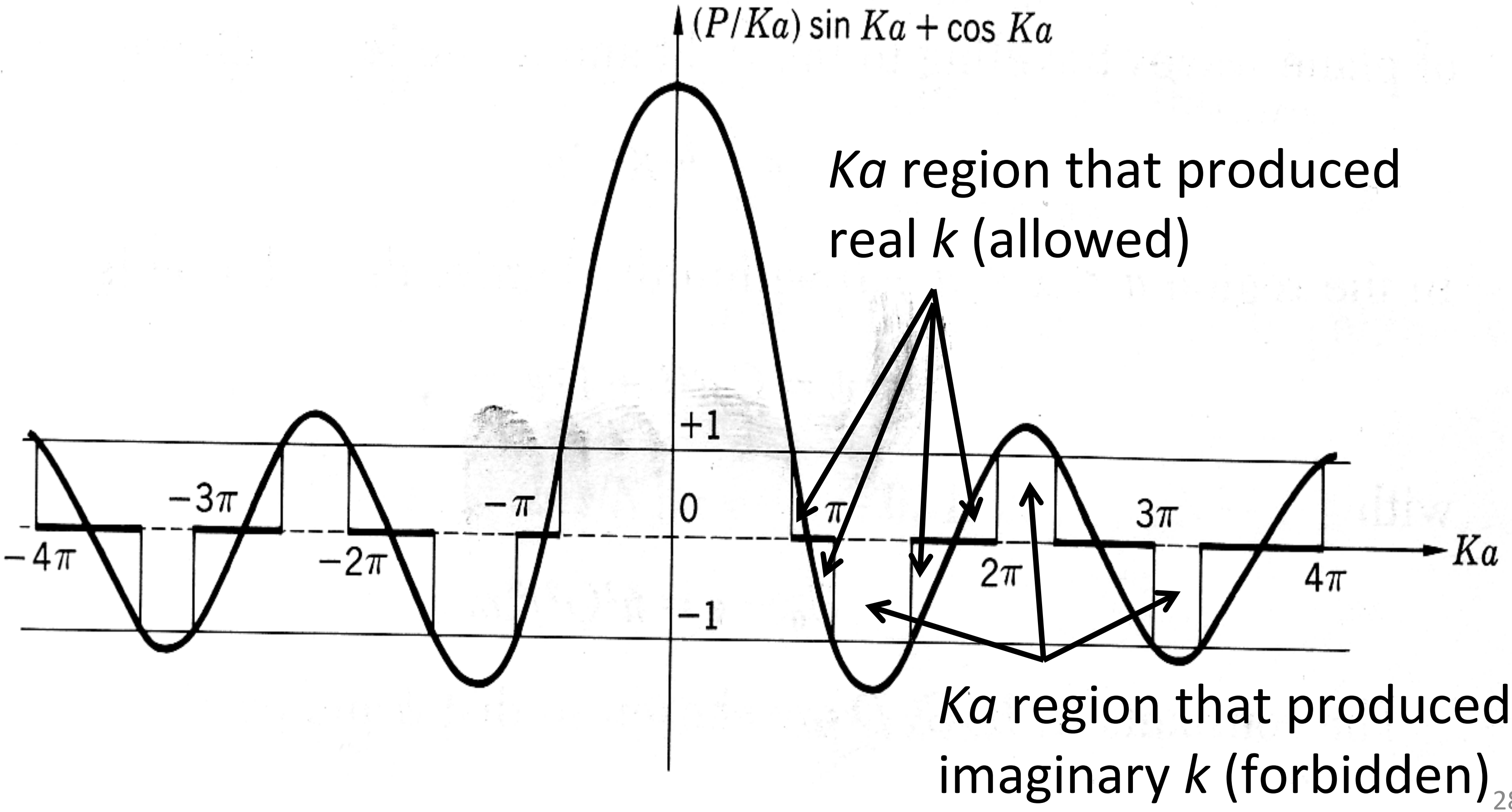
$$\cos ka = \cos Ka$$

$$k = K \qquad \text{(free electron)}$$

- If $P \to \infty \;\; (V_0 \to \infty)$, infinite barrier

(quantized electron energy)

- Let us consider P with a finite value, $P = 3\pi/2$
- The graph of $(P/Ka)\sin Ka + \cos Ka$ versus Ka has the form



- Equation (12.16) has a solution for *k* (real *k*) when

$$-1 < (P/Ka)\sin Ka + \cos Ka < +1 \qquad (12.17)$$

which is

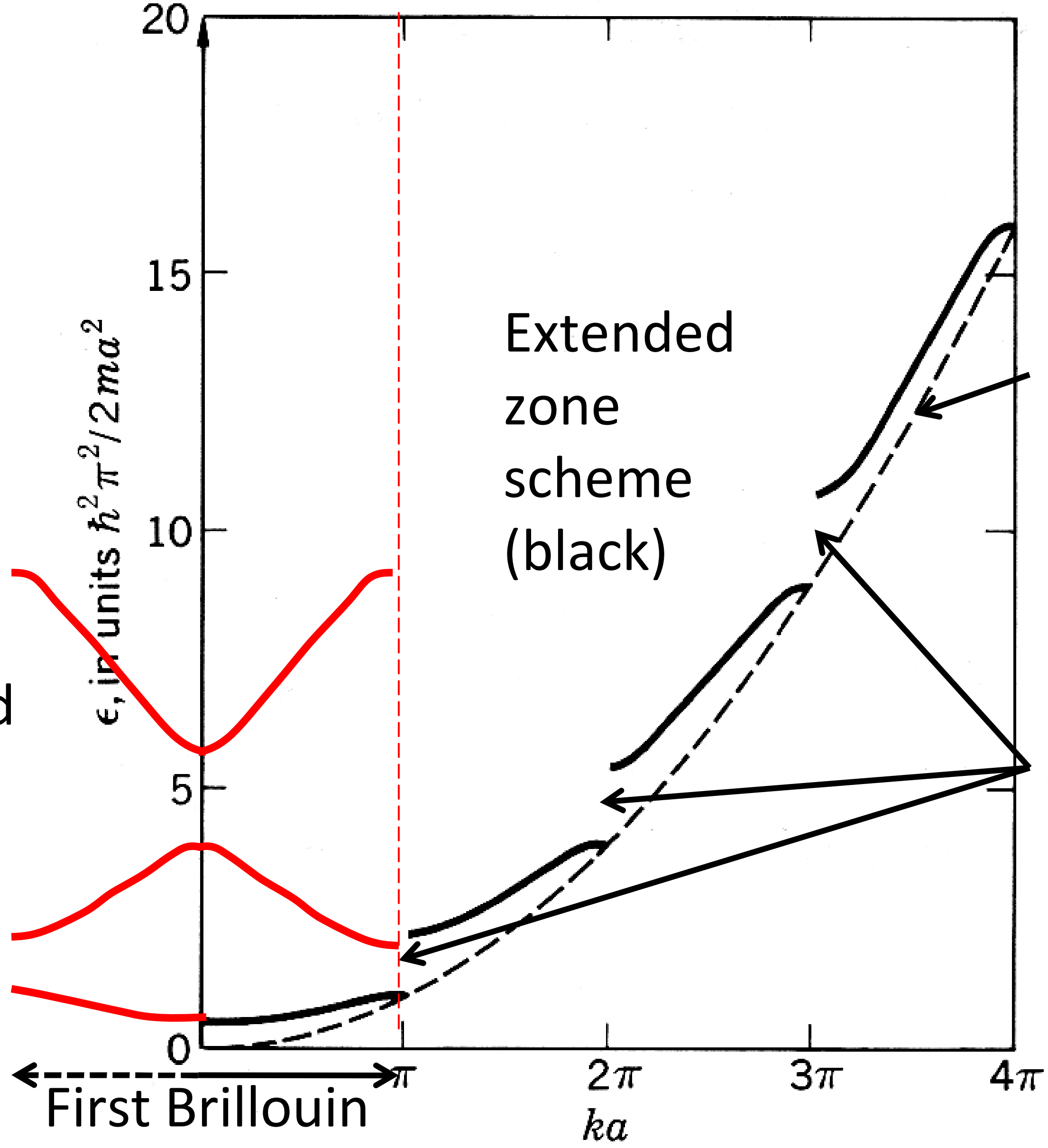
$$-1 < \cos ka < +1 \qquad (12.18)$$

- Therefore the allowed overall electron wave vectors *k* (real) have values between

$$n\frac{\pi}{a} < k < (n+1)\frac{\pi}{a}$$

- Thus the graph for the overall electron energy has the following shape

Reduced zone scheme (red)



First Brillouin zone

Free electron

Forbidden energy or forbidden gap for $E_{overall}$ of which k is imaginary and occurs at the boundary of Brillouin zones

12.5 Effective mass of electron

- Group velocity for an electron wave function is given as

$$\boldsymbol{v}_g = \frac{d\omega}{d\boldsymbol{k}} \qquad (12.19)$$

where the angular frequency

$\omega = \mathcal{E}/\hbar = \text{electron energy}/\hbar$

- Therefore

$$\boldsymbol{v}_g = \frac{1}{\hbar}\frac{d\mathcal{E}}{d\boldsymbol{k}} \qquad (12.20)$$

- Consider an electron in a periodic solid and an external electric field ***E*** acting on the electron
- The external force on the electron is

$$\boldsymbol{F} = \hbar \frac{d\boldsymbol{k}}{dt} = -e\boldsymbol{E} \qquad (12.21)$$

$$\frac{d\boldsymbol{k}}{dt} = -\frac{e\boldsymbol{E}}{\hbar} \qquad (12.22)$$

- The acceleration of the electron is given as

$$\boldsymbol{a} = \frac{d\boldsymbol{v}_g}{dt} = \frac{1}{\hbar}\frac{d^2\mathcal{E}}{d\boldsymbol{k}^2}\frac{d\boldsymbol{k}}{dt} = \frac{1}{\hbar}\frac{d^2\mathcal{E}}{d\boldsymbol{k}^2}\left(-\frac{e\boldsymbol{E}}{\hbar}\right)$$

$$\boldsymbol{a} = \left(-\frac{e\boldsymbol{E}}{\hbar^2}\right)\frac{d^2\mathcal{E}}{d\boldsymbol{k}^2} \equiv -\frac{e\boldsymbol{E}}{m^*} \qquad (12.23)$$

where m^* is the effective mass

- Compare Eq. (12.23) with the equation for the acceleration of free electron in an electric field ***E***

$$\boldsymbol{a} = \frac{\boldsymbol{F}}{m} = -\frac{e\boldsymbol{E}}{m} \qquad (12.24)$$

- Thus the magnitude of electron effective mass in a periodic solid is

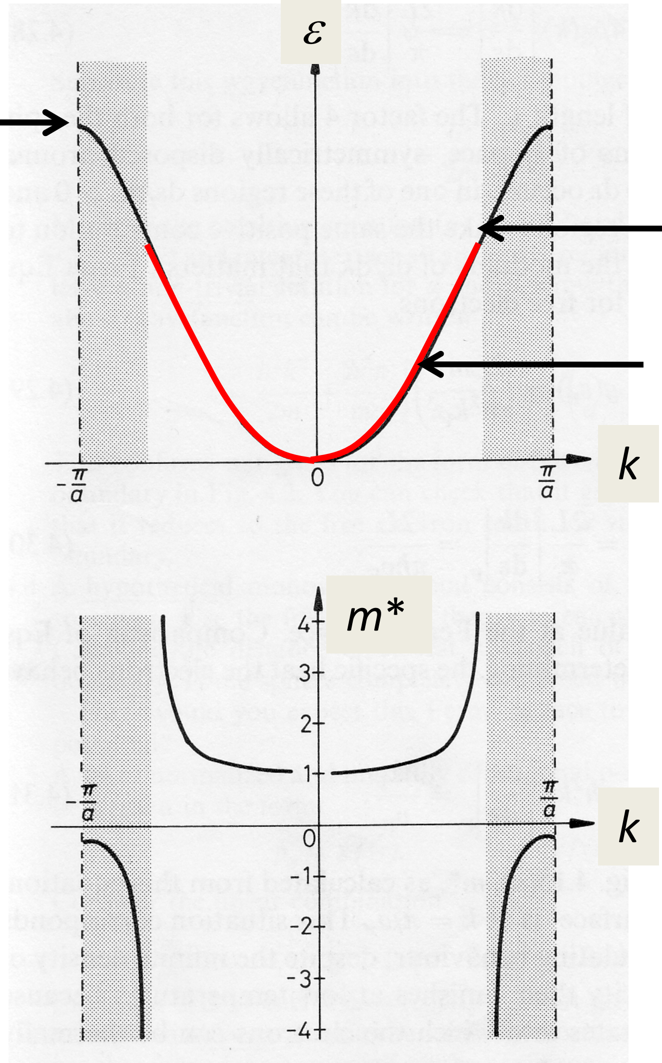
$$m^* = \hbar^2 \frac{1}{\frac{d^2\mathcal{E}}{dk^2}}$$

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2\mathcal{E}}{dk^2} \qquad (12.25)$$

- $1/m^*$ is responsible for the curvature of the graph of $\mathcal{E}$ versus k at the edge of the Brillouin zone (via the periodic potential)

$$\frac{d\mathcal{E}}{dk} = 0$$

$$\frac{d^2\mathcal{E}}{dk^2} \neq 0$$

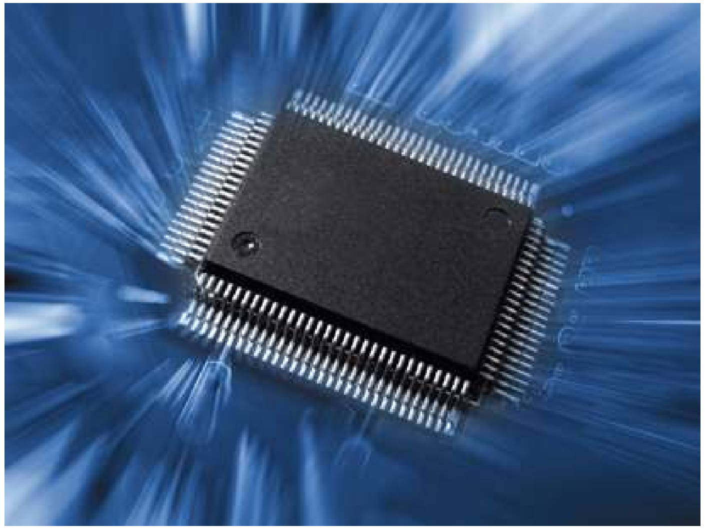


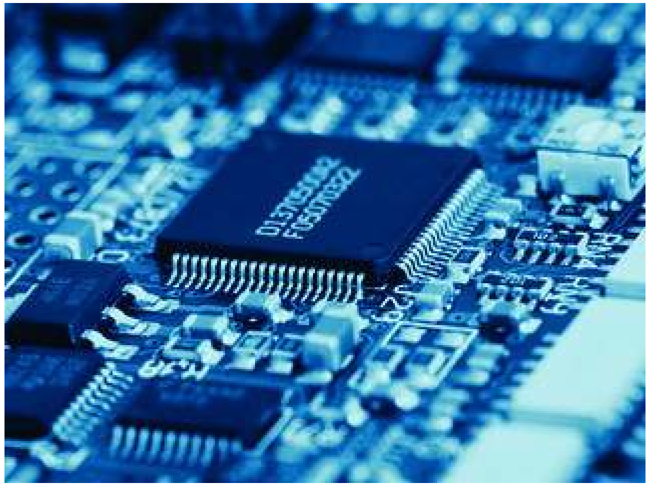
$$\frac{d^2\mathcal{E}}{dk^2} = 0$$

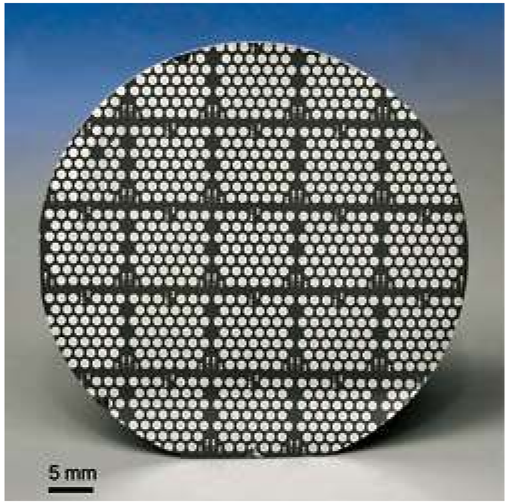
Like free electron (red)

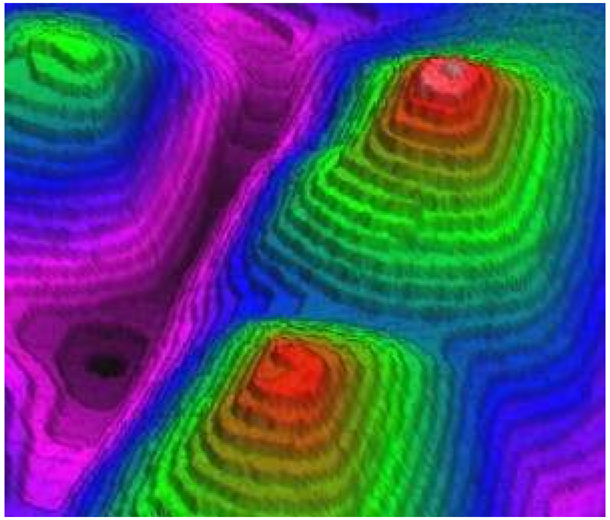
$$m^* \propto \frac{1}{\frac{d^2\mathcal{E}}{dk^2}}$$

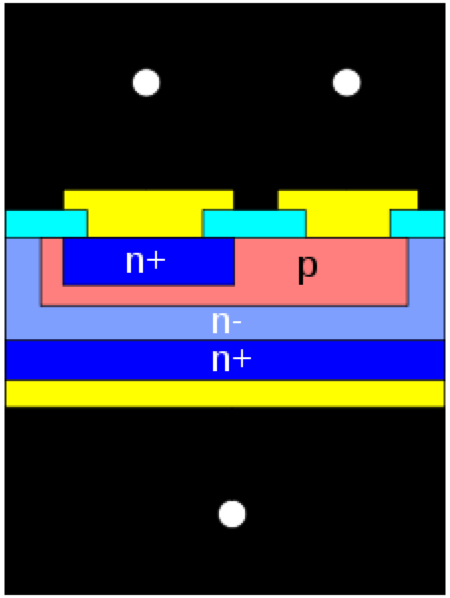
What Come Into Your Mind When I Mention SEMICONUCTOR?











What is Semiconductor?

- definition from Whatis.com & siliconfareast.com

- A semiconductor is a substance, usually a solid chemical element or compound, that can conduct electricity under some conditions but not others, making it a good medium for the control of electrical current.
- Its conductance varies depending on the current or voltage applied to a control electrode, or on the intensity of irradiation by infrared (IR), visible light, ultraviolet (UV), or X rays.
- The specific properties of a semiconductor depend on the impurities, or *dopants*, added to it.
- ***Doping*** is the process of adding impurities to an intrinsic semiconductor to increase its ability to conduct electricity.
- The difference in the number of valence electrons between the doping material, or dopant, and host semiconductor results in negative (n-type) or positive (p-type) carriers of electricity.

- The dopant is known as an acceptor atom if it 'accepts' an electron from the semiconductor atom.
- It is known as a donor atom if it 'donates' an electron to the semiconductor atom.
- An *N-type* semiconductor carries current mainly in the form of negatively-charged electrons, in a manner similar to the conduction of current in a wire.
- A *P-type* semiconductor carries current predominantly as electron deficiencies called holes.
- A hole has a positive electric charge, equal and opposite to the charge on an electron.
- In a semiconductor material, the flow of holes occurs in a direction opposite to the flow of electrons.
- In an intrinsic semiconductor such as silicon, the valence electrons of an atom are paired and shared with other atoms, making covalent bonds that hold the crystal together.

- Under such circumstances, these valence electrons are not free to move around as electrical current.
- Temperature or light **excites the valence electrons** out of these bonds, freeing them to conduct current.
- The vacant positions left behind by the freed electrons, also known as ***holes***, can move around as well, contributing to the flow of electricity.
- The energy needed to excite the electron and hole is known as the ***energy gap***.
- Elemental semiconductors include antimony, arsenic, boron, carbon, germanium, selenium, silicon, sulfur, and tellurium.
- Silicon is the best-known of these, forming the basis of most integrated circuits (ICs).
- Common semiconductor compounds include gallium arsenide, indium antimonide, and the oxides of most metals.

Crystal Structure & Bonding of Semiconductor

- Semiconductors include a large number of substances of widely different chemical and physical properties.
- These materials are grouped into several classes of similar behavior, the classification being based on the position in the periodic table of the elements.
- The best-known class is the Group IV semiconductors - C (diamond), Si, Ge, - all of which lie in the fourth column of the periodic table.
- The elemental semiconductors all crystallize in the diamond structure.
- The diamond structure has an fcc lattice with a basis composed of two identical atoms, and is such that each atom is surrounded by four neighboring atoms, forming a regular tetrahedron.
- Group IV semiconductors are covalent crystals, i.e., the atoms are held together by covalent bonds.
- These bonds consist of two electrons of opposite spins distributed along the line joining the two atoms.
- The covalent electrons forming the bonds are hybrid sp^3 atomic orbitals.

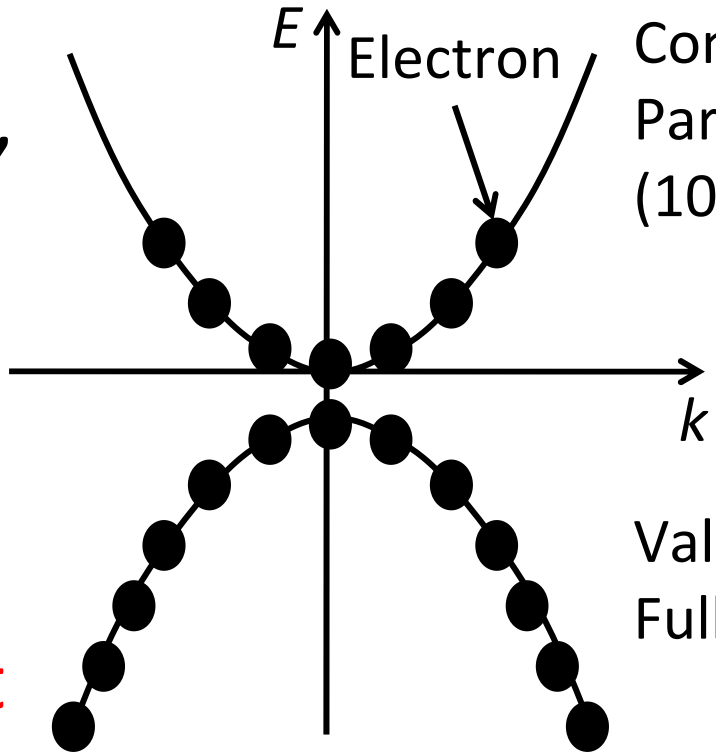
Crystal Structure & Bonding of Semiconductor -cont

- Another important group of semiconductors is the Group III-V compounds, so named because each contains two elements, one from the third and the other from the fifth column of the periodic table.
- The best-known members of this group are GaAs and InSb (indium antimonite), but the list also contains compounds such as GaP, InAs, GaSb, and many others.
- These substances crystallize in the zincblend structure which is the same as the diamond structure, except that the two atoms forming the basis of the lattice are now different.
- Thus, in GaAs, the basis of the fcc lattice consists of two atoms, Ga and As.
- Because of this structure, each atom is surrounded by four others of the opposite kind, and these latter atoms form a regular tetrahedron, just as in the diamond structure.

13 Semiconductor Crystals

13.1 Energy bands for metals, insulators and semiconductors

- At temperature $T = 0$ K (reduced zone scheme)
- Metals
  - In an electric field, the electrons in the conduction band are free to move, thus producing current



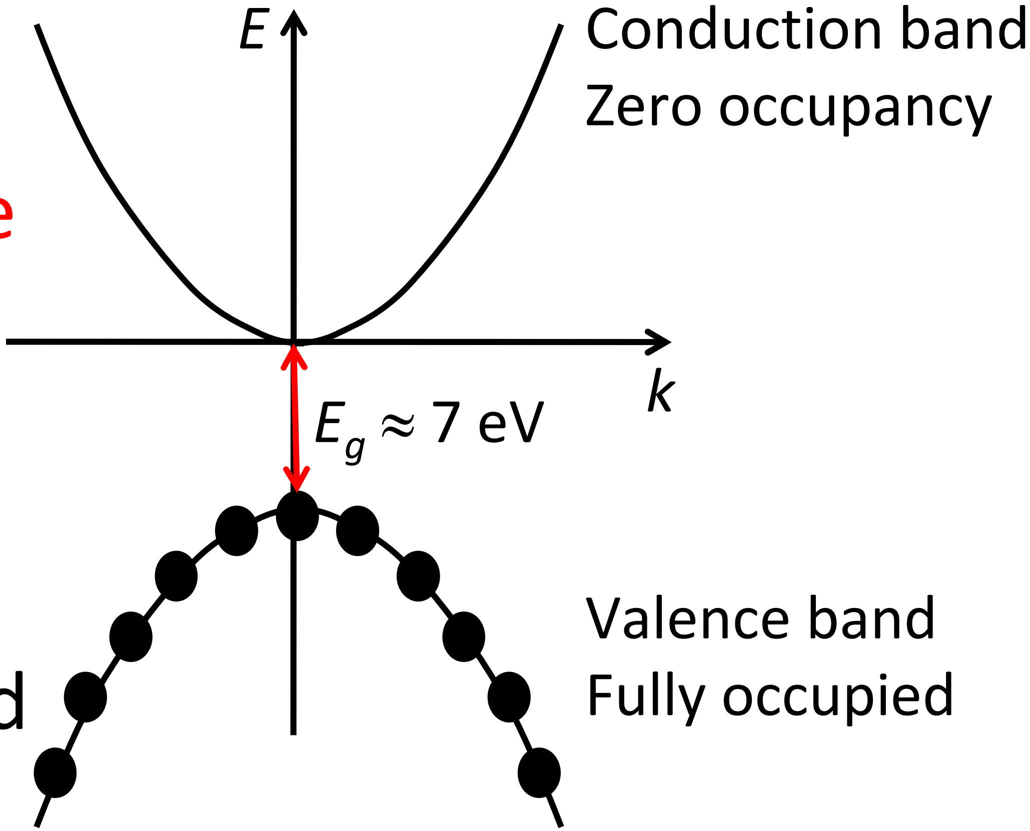
Conduction band
Partially filled
(10 – 90%)

Valence band
Fully filled

- $\rho_{300\,K} \approx 10^{-6}\,\Omega\text{cm}$

- Insulators

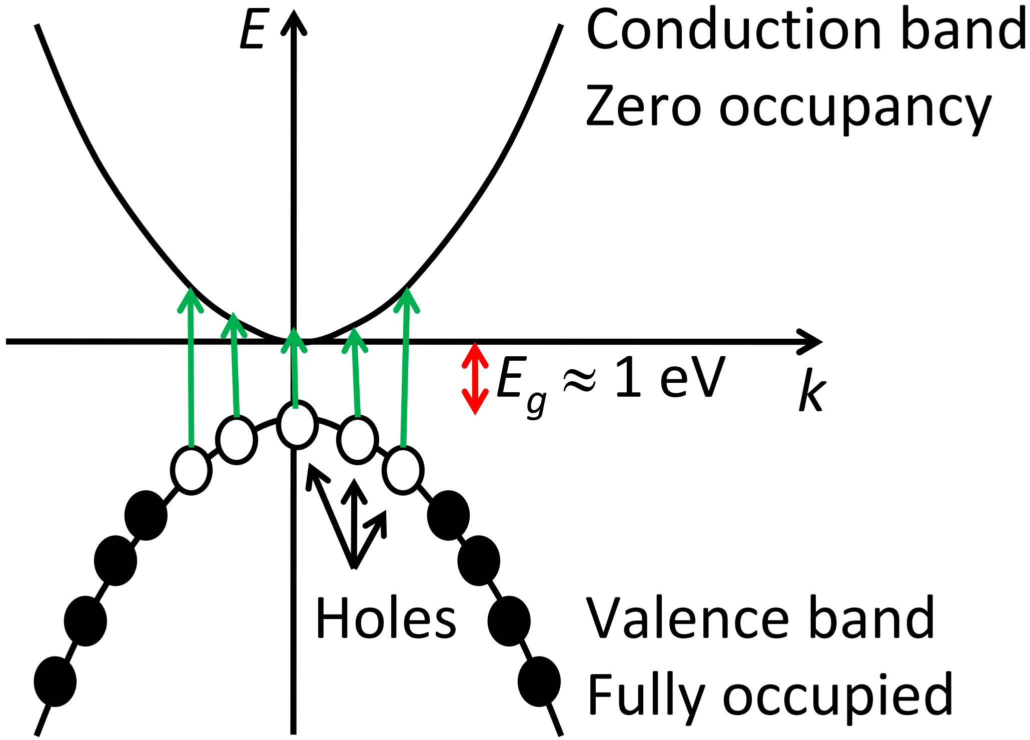
- When temperature is increased, there is no transition from valence band to conduction band because E_g is large



- A complete band does not carry electric current even with the presence of an electric field

- $\rho_{300\,K} \approx 10^{14} \rightarrow 10^{22}\,\Omega\text{cm}$

- Semiconductors
  - At temperature T = 0 K, it is an insulator
  - When temperature T is increased, electrons in the valence band are thermally excited to the conduction band and become mobile
  - Excitation of electrons creates holes in the valence band

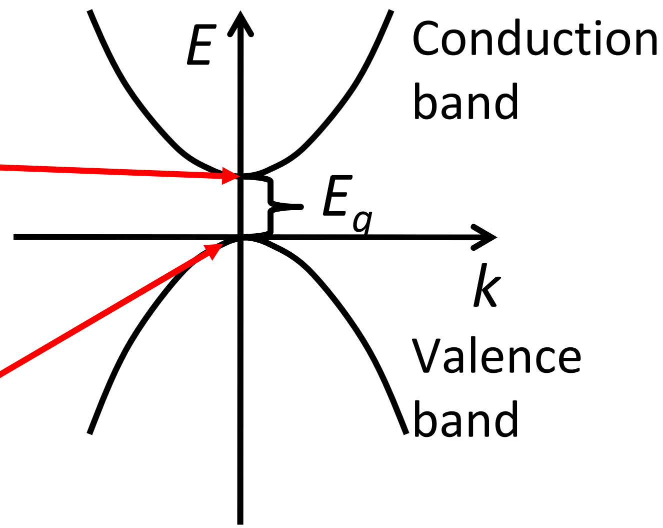


- The electrons in the conduction band and holes in the valence band are responsible for the electrical conduction in the semiconductor
- $\rho_{300\ K} \approx 10^{-2} \rightarrow 10^{9}\Omega\text{cm}$

13.2 Semiconductor energy bands

Lowest point of the conduction band is called the edge of the conduction band

Highest point of the valence band is called the edge of the valence band



- The energy difference between the conduction band edge and valence band edge is called the energy band gap E_g
- The energy of the conduction band is given as

$$E_c(\boldsymbol{k}) = E_g + \frac{\hbar^2 k^2}{2m_e^*}$$

where $\boldsymbol{k}$ is the wave vector and m_e^* the electron effective mass

- The zero energy level is at the edge of the valence band
- The energy of the valence band is given as

$$E_v(\boldsymbol{k}) = -\frac{\hbar^2 k^2}{2m_h^*}$$

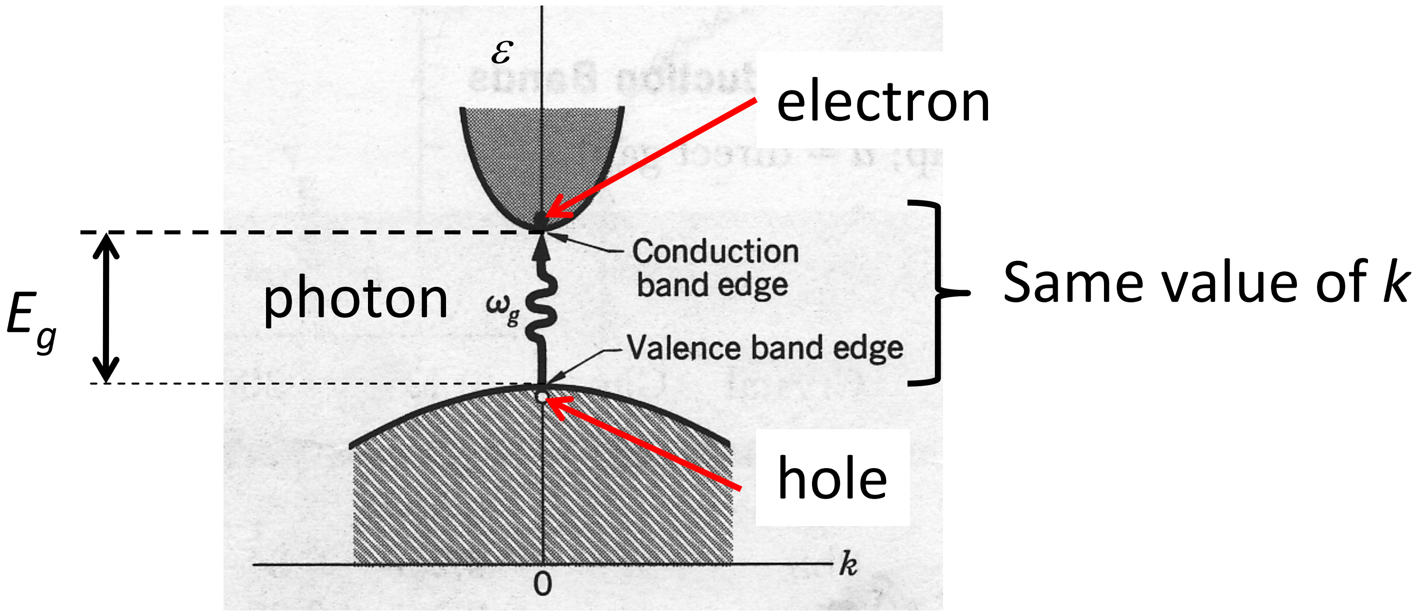
where m_h^* is the effective mass of hole

- Energy gap can vary with
  - Temperature (small changes)
  - Pressure (due to changes to the lattice constant)

13.3 Energy gap

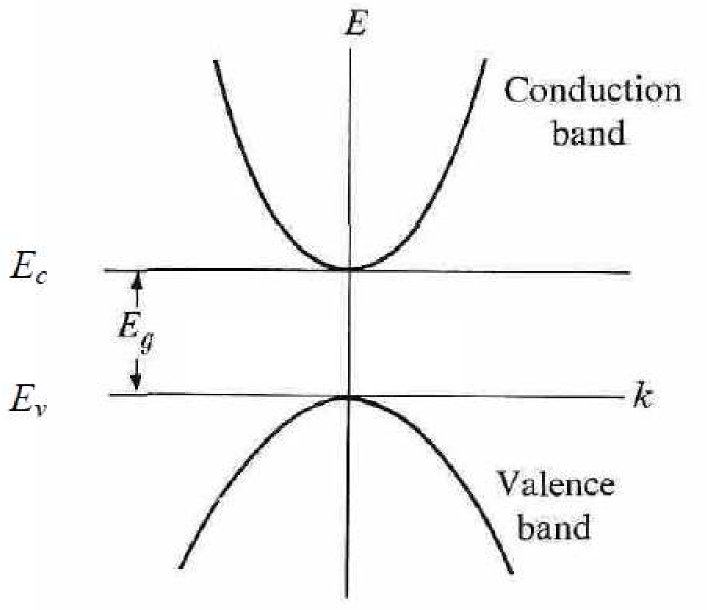
- Direct energy gap

- Occurs when the edge of the conduction band and the edge of the valence band are at the same value of k



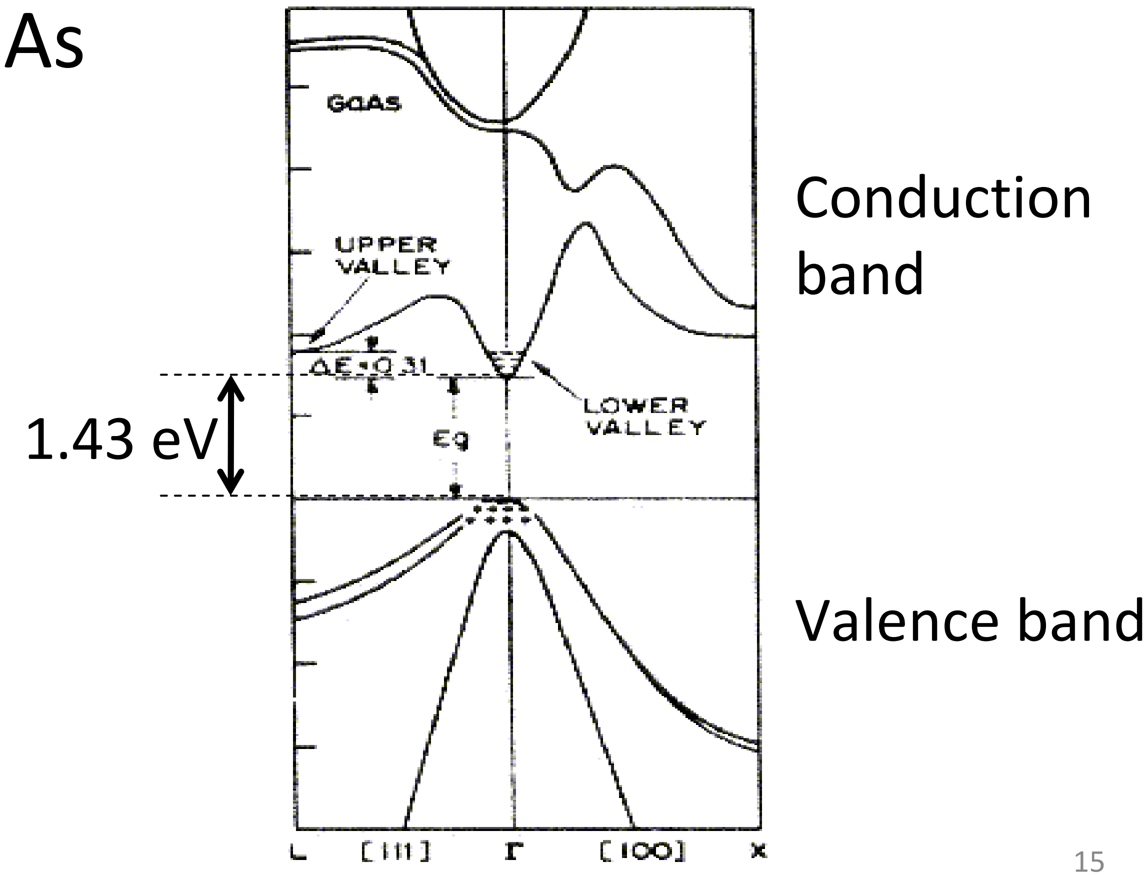
- The value of E_g can be obtained using optical absorption (photon energy absorbed by electron)
- In this direct absorption process, a photon with very small wave vector is absorbed to create an electron (conduction band) and a hole (valence band)

- The energy gap for a semiconductor varies with temperature, but the variation is usually slight.
- That a variation with temperature should exist at all can be appreciated from the fact that the crystal, when it is heated, experiences a volume expansion, and hence a change in its lattice constant.
- This, in turn, affects the band structure, which is a sensitive function of the lattice constant.
- The band structure in figure beside is the simplest possible structure.
- Band structures of real semiconductors are somewhat more complicated.



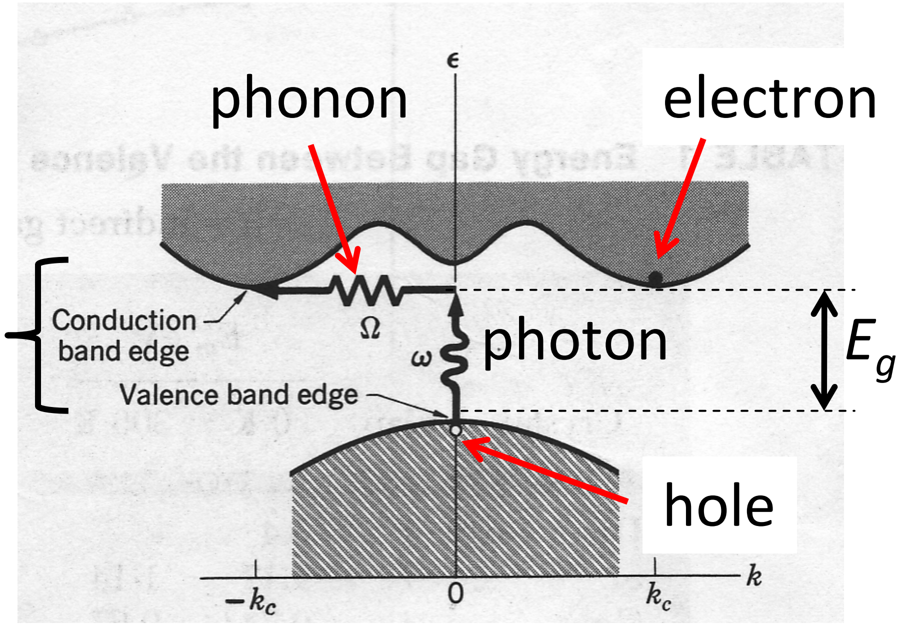
Band structure in a semiconductor.

- The difference in wave vector between electron and hole is essentially zero
- The direct energy band gap, $E_g = \hbar\omega_g$, is determined by the threshold frequency ω_g
- For example GaAs



- Indirect energy gap
  - The conduction band edge and valence band edge are at different values of k

Different values of k



  - The change in wave vector associated with the direct photon absorption is essentially $\Delta k = 0$

- While the electron transition from valence band edge to the conduction band edge requires a large change in *k*
- This can be achieved if phonon (lattice vibration) energy is also absorbed by the electron
- This transition process is called indirect absorption due to the indirect energy gap

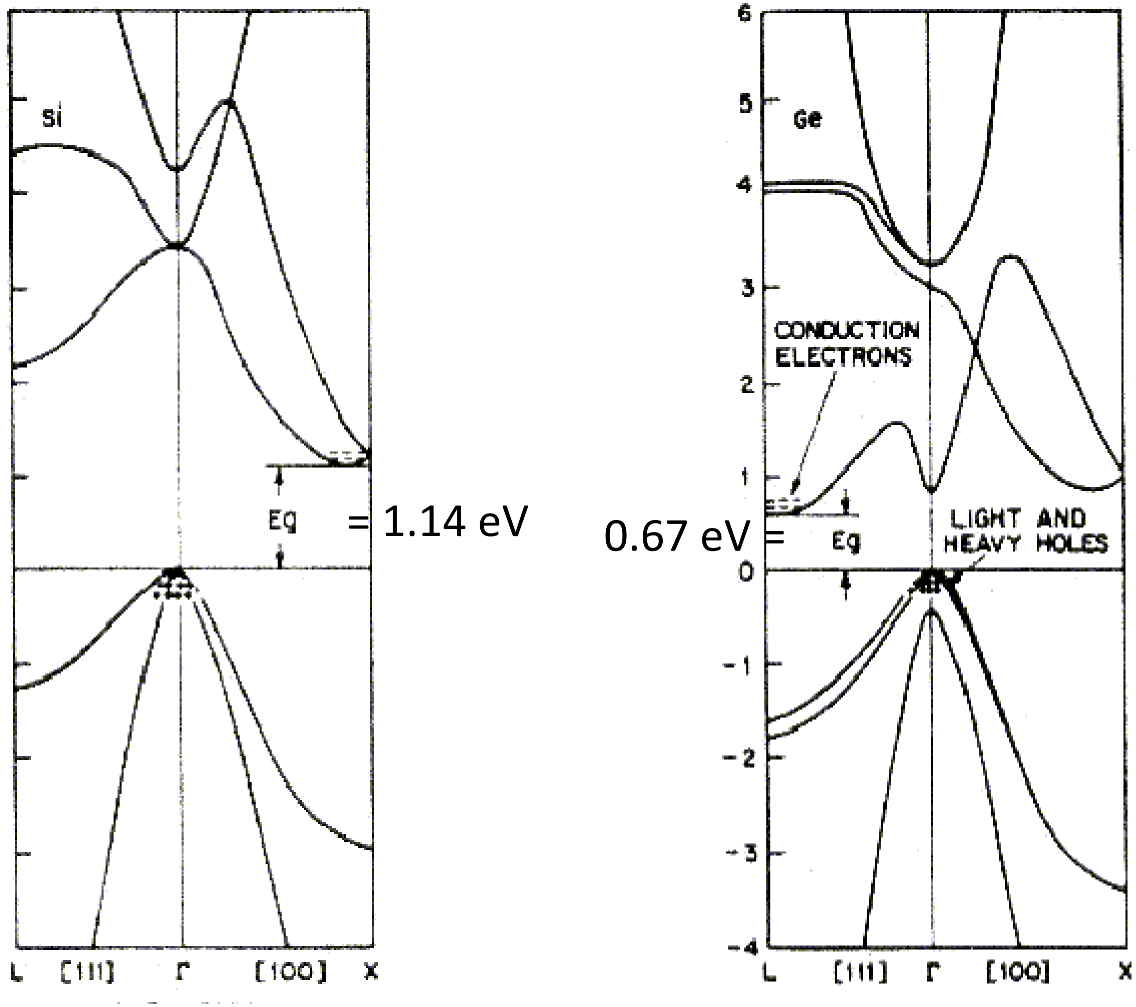
$$E_g = \hbar\omega + \hbar\Omega$$

$$\hbar\omega = E_g - \hbar\Omega \qquad \text{(phonon absorbed)}$$

$$\hbar\omega = E_g + \hbar\Omega \qquad \text{(phonon emitted)}$$

where Ω is the phonon frequency

- For example Si and Ge



Conduction band

Valence band

13.4 Holes

- In semiconductors, electrons that are excited to the conduction band leave vacancies or holes which are positively charged in the valence band
- The electrons and holes are called free carriers, and are responsible for the current flow in the semiconductor
- The number of free carriers is important because it determines the electrical conductivity of a semiconductor
- The electrical conductivity

  $$\sigma = (ne\mu_e + pe\mu_h)$$

where n and p are electrons and holes concentration, respectively, while μ_e and μ_h are electrons and holes mobility, respectively

- Mobility is

$$\mu = \frac{|\upsilon|}{E} = \frac{|\text{drift velocity}|}{\text{electric field}}$$

- μ is defined as positive for electrons and holes even though υ_e and υ_h are of opposite directions
- For a charge q, $|\upsilon| = q\tau E/m$, thus

$$\mu_e = e\tau_e/m_e$$

- and

$$\mu_h = e\tau_h/m_h$$

13.5 Intrinsic carrier concentration

- In pure semiconductors, electrons and holes carrier concentrations are the same
- This is due to each electron being excited to the conduction band creates a hole in the valence band
- The semiconductor is called an intrinsic semiconductor
- For $E_g >> k_BT$

$$np = 4\left(\frac{k_BT}{2\pi\hbar^2}\right)^3 (m_e m_h)^{3/2} e^{-E_g/k_BT} \qquad (13.1)$$

where m_e and m_h are the effective masses of electrons and holes, respectively

- Therefore for intrinsic semiconductors, the carrier concentrations are

$$n_i = p_i = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} e^{-E_g/2k_B T}$$

(13.2)

- n_i and p_i rapidly increase exponentially when the temperature is increased

$$\frac{1}{e^{E_g/2k_B T}} \uparrow \quad \text{when T} \uparrow$$

- The Fermi energy level in the energy gap E_g is

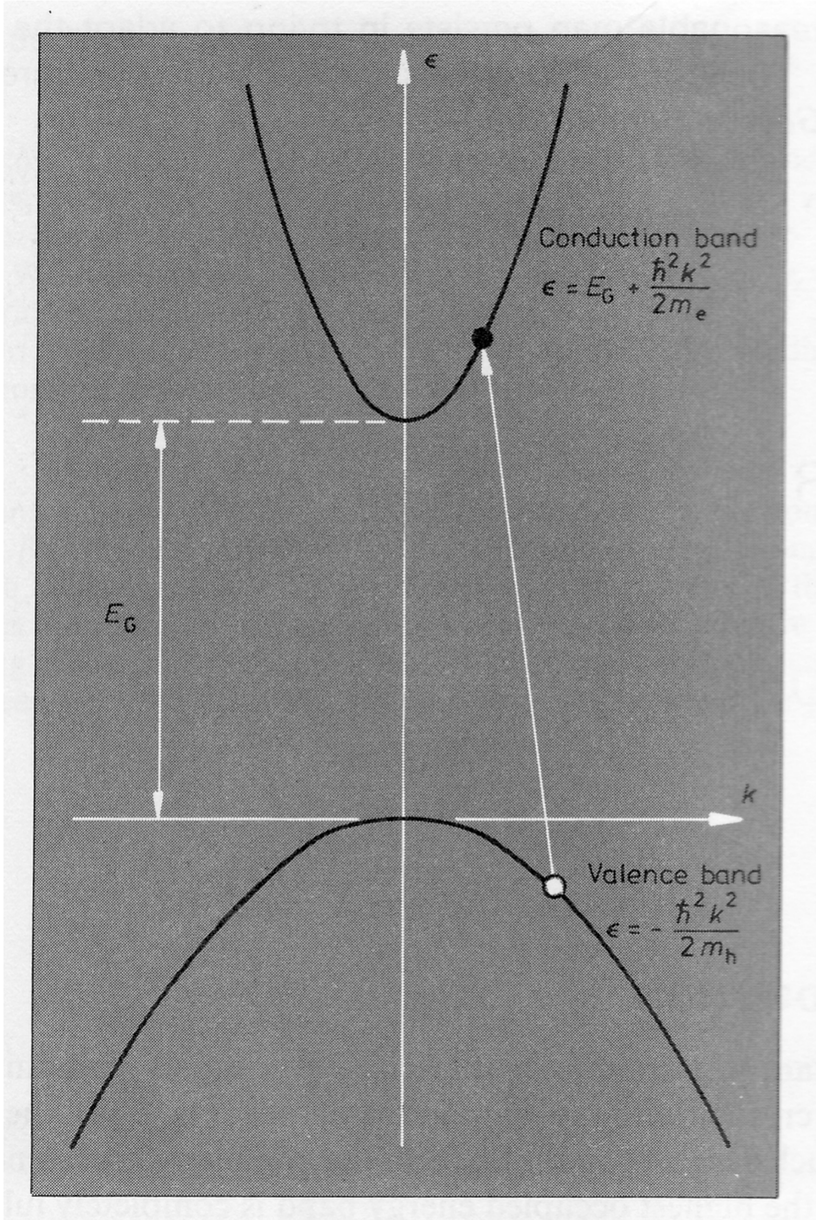
$$E_F = \frac{1}{2}E_g + \frac{3}{4}k_B T \ln\left(\frac{m_h}{m_e}\right) \quad (13.3)$$

- If the electron mass equals the hole mass, $m_e = m_h$, then

$$E_F = \frac{1}{2}E_g \quad (13.4)$$

- The Fermi level is in the middle of the gap
- The energy bands of "pure" or intrinsic semiconductors do not show energy levels associated with impurities (donors or acceptors) and lattice imperfections

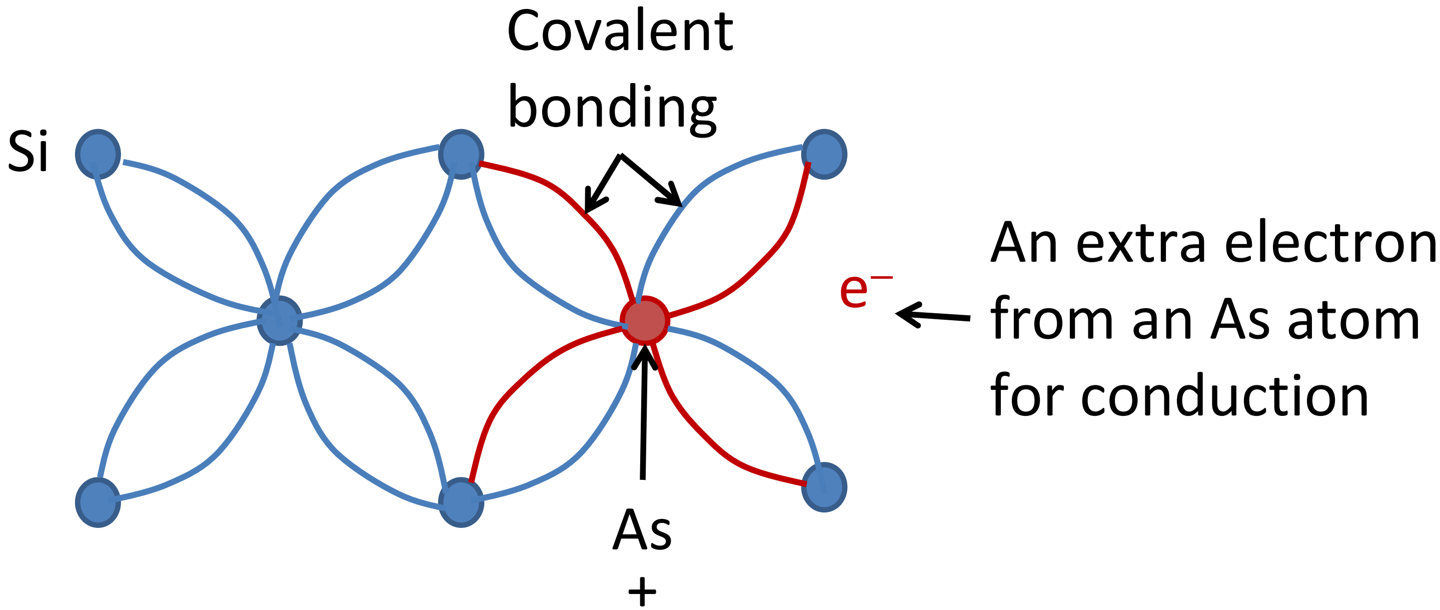
- Energy bands of an intrinsic semiconductor



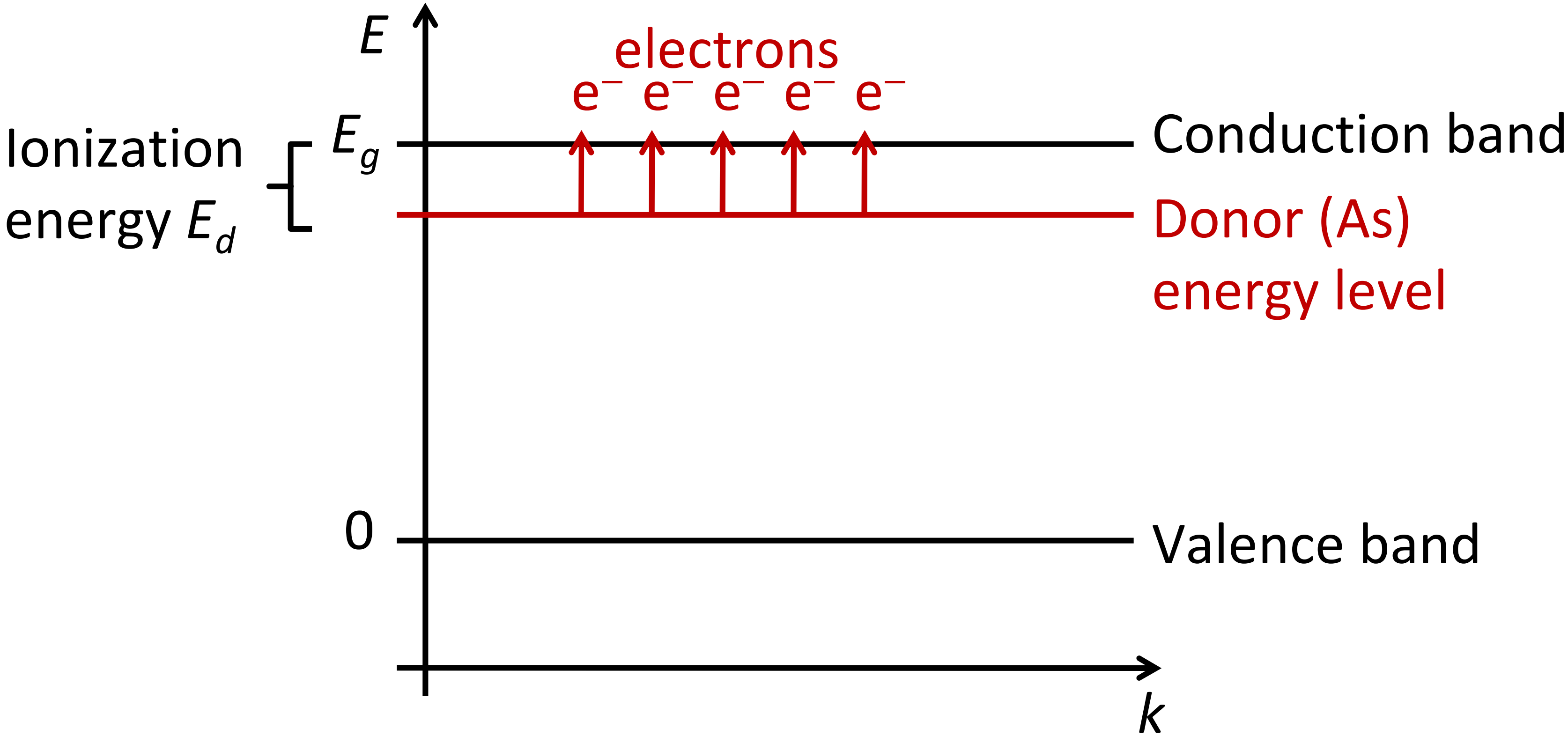
13.6 Extrinsic carrier concentration

- A semiconductor is said to be extrinsic when it is not pure (there exist impurities)
- Impurities can provide extra electrons or holes as free carriers
- Thus producing higher values for electrical conductivity compared to intrinsic semiconductors
- There are two types of extrinsic semiconductors, *n*-type and *p*-type
- Consider the semiconductor Si

- *n*-type Si (with As (arsenic) as the impurity)

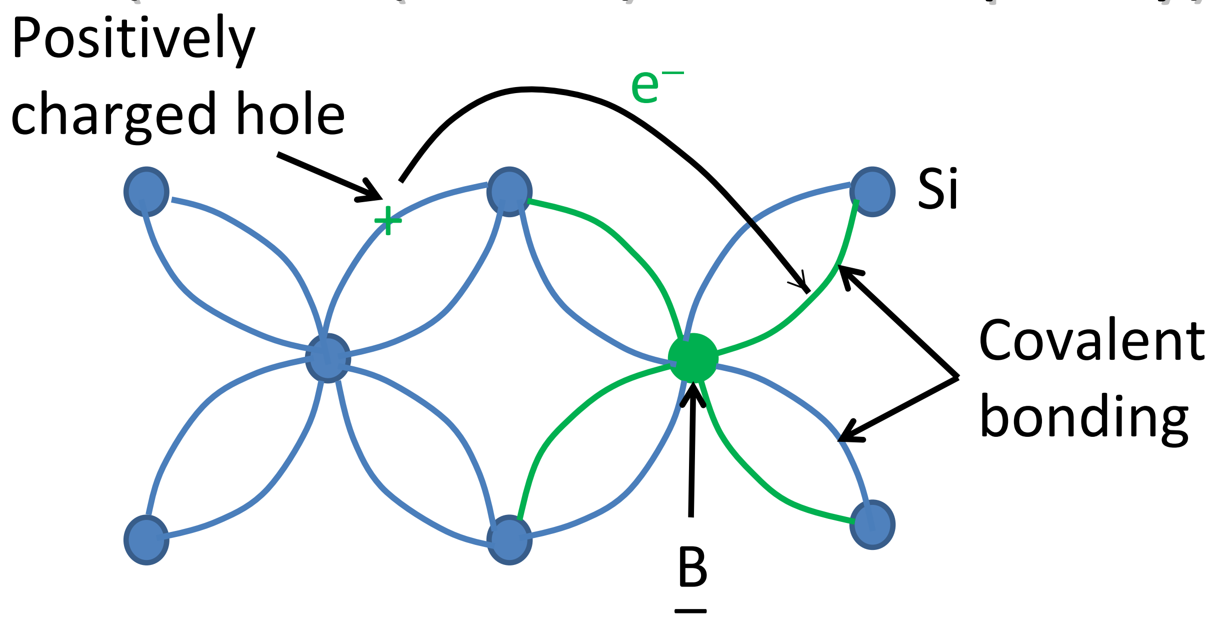


- Si atom has 4 valence electrons
- As atom has 5 valence electrons
- As atom is called a donor because after ionization it donates one electron to the conduction band of Si



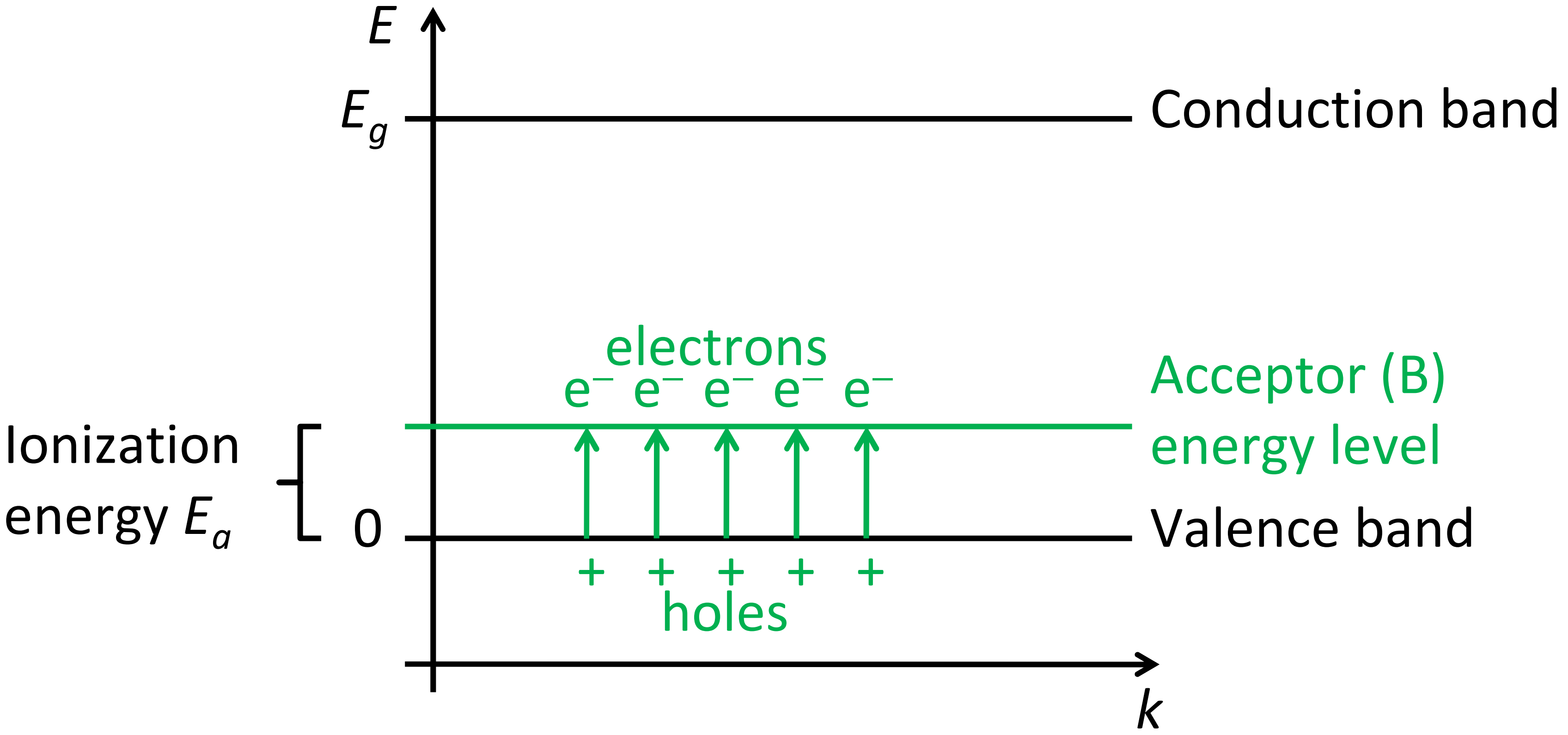
- Therefore electrical conductivity is controlled by the negatively charged electrons and the extrinsic semiconductor is *n*-type

- *p*-type Si (with B (boron) as the impurity)



- Si atom has 4 valence electrons
- B atom has 3 valence electrons
- To complete the B – Si bonding, an electron from Si – Si covalent bonding is used, thus a hole exists at that Si – Si bonding

- B atom is called an acceptor because when there is an ionization it receives electron from the valence band of Si and a hole is created



- Here the electrical conductivity is controlled by the positively charged holes and the extrinsic semiconductor is *p*-type
- Conduction electron concentration from the donors (no acceptors) is given by

$$n \approx \left\{2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} N_d\right\}^{1/2} e^{-E_d/2k_BT} \qquad (13.5)$$

$$n \approx 2^{1/2}\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/4} N_d^{\,1/2} e^{-E_d/2k_BT} \qquad (13.6)$$

where N_d is the donors concentration

- The conduction hole concentration is similar to Eq. (13.6) if there are no donors